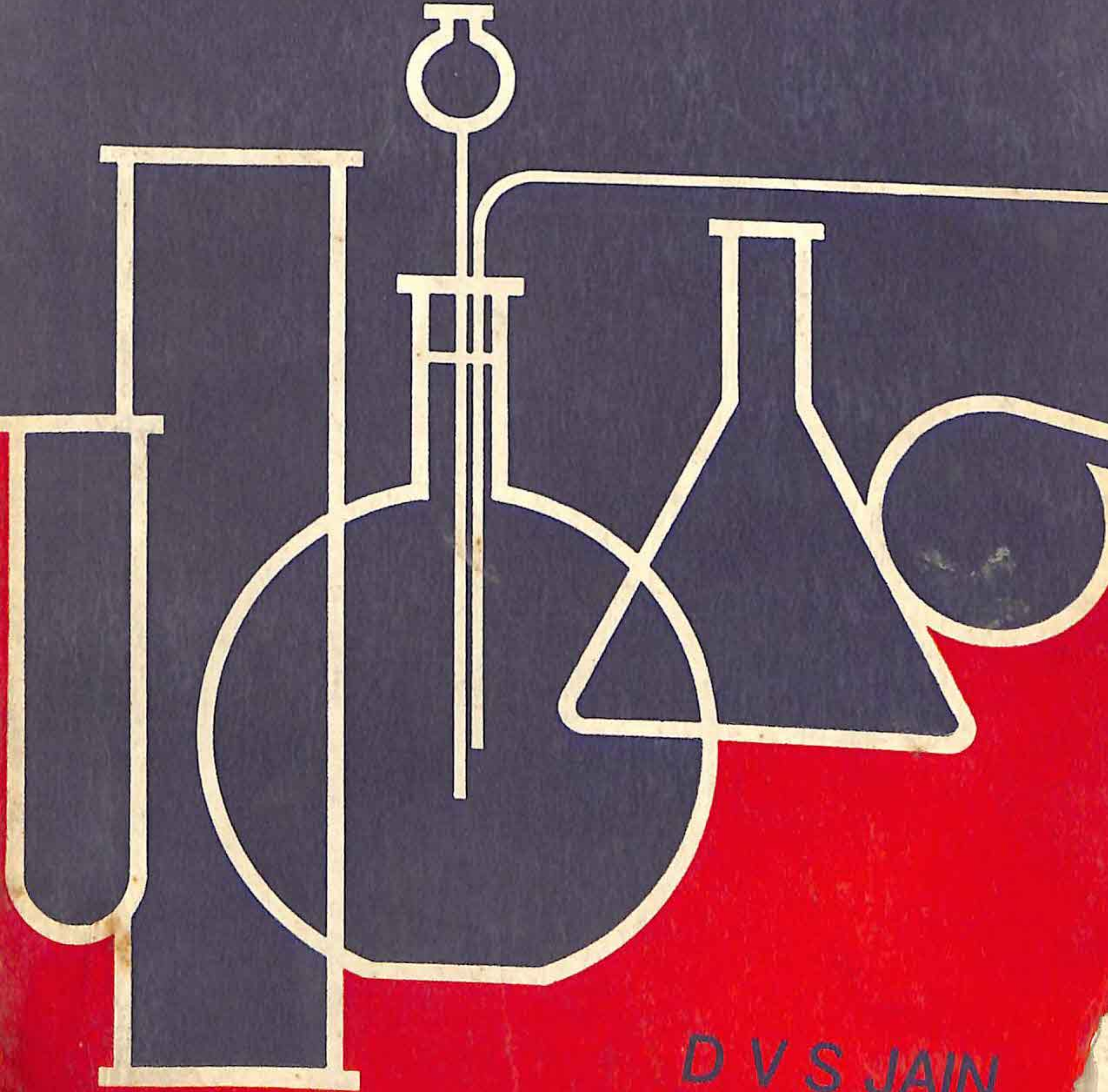
PHYSICAL CHEMISTRY

Principles and Problems



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Preface

Physical chemistry forms an integral part of nearly all the branches of science, technology and engineering. Even in an elementary course of physical chemistry, a large number of concepts and definitions have to be introduced. It is no wonder that students, specially those who are somewhat weak in physics and mathematics, find it difficult to grasp the subject. From our class-room experience with students, we have found that they learn physical chemistry more easily if they solve numerical problems based on the applications of these concepts. Furthermore, the definitions and concepts have to be learnt precisely. And also exercises involving the choice of correct answer from seemingly similar statements definitely sharpens the understanding of the subject.

This book aims at preparing students to learn the basics of physical chemistry through numerical problems and quiz questions. The book is divided into 23 chapters. Each chapter provides brief but sufficient coverage to definitions of quantities, development of concepts and derivation of important equations. These are further elucidated by suitable solved examples as the subject is developed. This also gives the reader a feeling for the magnitudes of various physico-chemical quantities. A set of problems is then included for the sake of practice. Finally, different types of quiz questions (multiple choice type, true or false statements type, and fill in the blanks type) are given so that the student can check if he has really understood the subject. The answers to different types of questions are given at the end of each chapter.

The book encourages the use of SI units. However, it is not uncommon to find data in non-SI units in various university and public examinations. Therefore, we have also given problems based on units other than SI units. We have explained the interconversion of units at the appropriate places.

The book is meant for BSc and BSc (Hons) students of Indian universities. It can also be of use to MSc students and candidates appearing for various public examinations. Suggestions and comments for the improvement of the book by the readers will be most welcome.

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1

Physico-Chemical Quantities and their Measurements in Physical Chemistry

Physical chemistry deals with the quantitative description of physico-chemical systems. In general such a system can be any part of the universe under study. In practice it consists of matter and/or radiation whose composition and other parameters are independent of time if it is in equilibrium. For a system not in equilibrium these change with time. The system may have boundaries which may be permeable to matter, energy and radiation or to any of their combinations. We shall learn more about these in later chapters. For a system in equilibrium this amounts to the specification of all physico-chemical quantities. These may be measured directly, or derived from other measured quantities. In some cases, they may be calculated theoretically. As the properties of the system are inter-related, it is not necessary to specify all of them for complete characterization. For time dependent systems, evolution in time has to be described. The rate at which they reach the equilibrium state constitutes an important area of physical chemistry.

1.1 UNITS

The measurement and calculation of physico-chemical properties and their interdependence is the essence of physical chemistry. The value of a physical quantity is always equal to the product of a numerical value and a unit. Naturally, we must have a convenient system of units for assigning numerical values to the measured or calculated quantities. Fortunately, it turns out that it is sufficient to define some *basic units* like time, mass, length, etc. Units for other quantities can be derived from these basic units and hence are called *derived units*. In recent years, scientists have generally agreed to the use of SI (Systeme Internationale) units, although a number of units used earlier are still in vogue. In this book we shall mainly use SI units. Problems and examples based exclusively on SI units are preceded by the indication (SI units). However, in view of the use of different types of units during the transition period, it is desirable to know the use of other units, especially their inter-conversion. The factors used in conversion are shown in bold letters to help the readers get acquainted with them.

1.2 SI UNITS

In this system, we define the following basic units:

Mass

The unit of mass is the *kilogram* (kg), defined as the mass of a platinum block stored at the International Bureau of Weights and Measures in France.

Length

The unit of length is the *metre* (m), defined as 1650763.73 wavelengths of the radiation of krypton-86 transition from $2p_{10}$ to $5d_5$, in vacuum.

Time

The unit of time is the *second* (s), defined as 9.192631770×10^9 periods of the radiation of Cs-133 transition between two hyperfine levels of the ground state.

Temperature

The unit of temperature is the *kelvin* (K) defined as the fraction 1/273.15 of the thermodynamic temperature of the triple point of water.

Current

The unit of current is the *ampere* (A) which is equal to the constant current maintained in two straight, parallel conductors of infinite length, and negligible cross section, placed 1 m apart in vacuum, which would produce a force equal to 2×10^{-7} newton per metre.

Amount

The *mole* (mol) is the amount of substance in a system which contains as many elementary entities as there are atoms* in 0.012 kg of carbon—12.

---

*The number is equal to the Avogadro number ($N_a = 6.022 \times 10^{23}$).

The elementary entities may be chosen as convenient, not necessarily as physically real individual particles. Thus, we have

$n(Cl)$ — amount of chlorine atoms

$n(Cl_2)$ — amount of chlorine molecules

$n\left(\frac{1}{5}KMnO_4\right)$ – amount of entities $\frac{1}{5}$ $KMnO_4$

For the amount of a substance, we use 'mole' in the text and 'mol' in equations and the symbol for its unit.

When the mole is used, the elementary entities must be specified. They may be atoms, molecules, ions, other particles or specified groups of such particles.

Luminosity

The unit of luminosity is the *candela* (cd), equal to the intensity in the perpendicular direction of the surface of 1/160000 square metres of a black body at the temperature of freezing platinum, under a pressure of 101325 newton per square metre.

Besides the above basic units, we also have the following supplementary SI units:

Plane Angle

The unit of plane angle is the *radian* (rad), equal to the angle between two radii of a circle which cut off, on the circumference, an arc of length equal to the radius.

Solid Angle

The unit of solid angle is the *steradian* (sr) which corresponds to an angle having its vertex at the centre of a sphere and cutting off an area, on the surface of the sphere, equal to that of a square with sides equal to the radius of the sphere.

1.3 DERIVED UNITS

The units of other physical quantities can be derived from the basic units explained above. The names and symbols of some selected quantities are given in Table 1.1

TABLE 1.1 *The Derived SI Units of Some Selected Physical Quantities*

Physical quantity	*Name*	*Symbol for SI unit*	*Definition of SI unit*
Force	newton	N	$kg\ m\ s^{-2}$
Pressure	pascal	Pa	$kg\ m^{-1}\ s^{-2} = N\ m^{-2}$
Energy	joule	J	$kg\ m^2\ s^{-2}$
Power	watt	W	$kg\ m^2\ s^{-3} = J\ s^{-1}$
Electric charge	coulomb	C	$A\ s$
Electric potential difference	volt	V	$kg\ m^2\ s^{-3}\ A^{-1} = J\ A^{-1}\ s^{-1}$
Electric resistance	ohm	Ω	$kg\ m^2\ s^{-3}\ A^{-2} = V\ A^{-1}$
Electric conductance	siemens	S	$kg^{-1}\ m^{-2}\ s^3\ A^2 = V^{-1}\ A$
Electric capacitance	farad	F	$A^2\ s^2\ kg^{-1}\ m^{-2} = A\ s\ V^{-1}$
Magnetic flux	weber	Wb	$kg\ m^2\ s^{-2}\ A^{-1} = V\ s$
Inductance	henry	H	$kg\ m^2\ s^{-2}\ A^{-2} = V\ A^{-1}\ s$
Magnetic flux density	tesla	T	$kg\ s^{-2}\ A^{-1} = V\ s\ m^{-2}$
Luminous flux	lumen	Lm	$Cd\ sr$
Illumination	lux	lx	$Cd\ sr\ m^{-2}$
Frequency	hertz	Hz	s^{-1}

1.4 PREFIXES

The SI units of some of the physical quantities discussed above are either too small or too large. To change the order of magnitude, these are preceded by certain prefixes. With the help of these prefixes it is possible to vary the unit from 10^{-18} to 10^{18}. These are listed in Table 1.2.

TABLE 1.2 *List of Prefixes*

Factor	*Symbol*	*Name*	*Origin*
10^{-1}	d	deci	Latin decimus (ten)
10^{-2}	c	centi	Latin centura (hundred)
10^{-3}	m	milli	Latin milli (thousand)
10^{-6}	μ	micro	Greek micro (small)
10^{-9}	n	nano	Greek nano (dwarf)
10^{-12}	p	pico	Italian pico (small)
10^{-15}	f	femto	Danish femten (fifteen)
10^{-18}	a	atto	Danish atten (eighteen)
10	da	deca	Greek deca (ten)
10^{2}	h	hecto	Greek ekatov (hundred)
10^{3}	k	kilo	Greek kilo (thousand)
10^{6}	M	mega	Greek mega (great)
10^{9}	G	giga	Greek giga (giant)
10^{12}	T	tera	Greek tera (monster)
10^{15}	P	peta	*
10^{18}	E	exa	*

*Tera can be considered to be derived from the tetra *minus* consonant 't' meaning $10^{3\times4} = 10^{12}$. Similarly, if we omit one consonant each from penta, it becomes peta ($10^{3\times5} = 10^{15}$), and hexa becomes exa ($10^{3\times6} = 10^{18}$).

1.5 IMPORTANT NOTES ON THE USE OF SI UNITS

In order to avoid confusion in the use of SI units, it is useful to remember the following:

- Unit combinations should be designated by means of either a dot or leaving space in between, e.g. m.K. (or m K) for metre kelvin and not mK which stands for milli kelvin.
- Words and symbols should not be in mixed forms. Thus, it is not proper to use J per mole; this should be written either as joule per mole or J mol^{-1}. If mathematical operations are indicated, only symbols should be used, e.g. J mol^{-1} and not joules mol^{-1}.
- Exponents also operate on prefixes, e.g.

$$1\ \text{cm}^2 = 10^{-4}\text{m}^2 \neq 10^{-2}\text{m}^2$$

$$1\ \text{mm}^3 = 10^{-9}\text{m}^3 \neq 10^{-3}\text{m}^3$$

1.6 MICROSCOPIC AND MACROSCOPIC APPROACHES TO PHYSICAL CHEMISTRY

There are two distinct approaches to the study of physical chemistry. In the first, called the *microscopic approach* (or *synthetic approach*), one starts with elementary particles. We first study the properties of atoms and molecules experimentally, by various spectroscopic and diffraction methods, or calculate them theoretically by the method of quantum mechanics. The collection of molecules lead to various states of aggregation like solid, liquid or gas. The properties of these can be calculated, in principle, by the methods of statistical mechanics, if we know the properties of the individual molecules and the nature of the interactions between them. This approach is aesthetically very beautiful and intellectually highly satisfying, but somewhat difficult to the uninitiated as it involves many abstract concepts.

In the second approach, called the *macroscopic approach* (or *analytical approach*), the matter in bulk is subjected to direct observations and the molecular basis of these observations is found. For example, Boyle's law for a gas, established on the basis of p–V measurements at constant temperature, is justified in terms of the kinetic theory of gases postulating that the gas consists of a large number of molecules moving in a random fashion. This approach is easier for the beginner as he can have a direct feeling for the system under investigation. Laws of thermodynamics are applicable to matter in bulk, without regard for structure. Nonetheless, both approaches are intimately connected, and a physical chemist moves back and forth from one approach to the other. Thus, the structure of matter and the energy distribution between molecules leads to a deep understanding of the laws of thermodynamics.

1.7 SOME COMMONLY USED NON-SI UNITS AND THEIR CONVERSION

The use of SI units has been accepted by most of the national and international societies in their publications. Most of the scientific journals recommend the use of SI units and symbols. However, some of the non-SI units (e.g. force, pressure and energy) are still in use. Moreover, physical quantities in older literature are also expressed in such units. It is, therefore, necessary to be familiar with some of the important units and their interconversion.

Force

N	dyn	kg f
1	10^5	0.102
10^{-5}	1	1.02×10^{-6}
9.81	9.81×10^5	1

Pressure

N/m^2	dyn/cm^2	$kg\ f/m^2$	bar	atm	torr (mm Hg)
1	10	0.102	10^{-5}	9.87×10^{-6}	7.5×10^{-3}
0.1	1	1.02×10^{-2}	10^{-6}	98.7×10^{-7}	7.5×10^{-4}
9.81	98.1	1	9.81×10^{-5}	9.68×10^{-5}	7.35×10^{-2}
10^5	10^6	1.02×10^4	1	0.987	7.5×10^2
1.01×10^5	1.01×10^6	1.03×10^4	1.01	1	7.6×10^2
1.33×10^2	1.33×10^3	13.6	1.33×10^{-2}	1.31×10^{-3}	1

Energy

J	erg	cal	eV	1 atm
1	10^7	0.2389	1.0364×10^{-5}	0.98689×10^{-2}
10^{-7}	1	2.389×10^{-8}	1.0364×10^{-12}	0.98689×10^{-9}
4.184	4.184×10^7	1	4.337×10^{-5}	0.04129
9.648×10^4	9.648×10^{11}	23.06×10^3	1	0.95223×10^3
11.961	1.1961×10^8	2.859	1.240×10^{-4}	1

where dyn stands for dyne, kg f for kilogram force, atm for atmosphere, cal for calorie, and eV for electron volt.

2

The Ideal Gas and its Kinetic Molecular Model

Matter exists in three different physical states: solid, liquid and gaseous. Of these, the gaseous state is the simplest and easily amenable to mathematical analysis. The measurable properties of gases, such as pressure, volume, temperature and mass, are interrelated through simple gas laws. Attempts were made to explain these laws in terms of the kinetic molecular theory of gases, and to study deviations from them.

2.1 GAS LAWS

Boyle's Law

This states that the volume (V) of a given mass of a gas at constant temperature (T) is inversely proportional to its pressure (p).

$$V \propto \frac{1}{p} \tag{2 1}$$

or $$pV = \text{constant (at constant T and mass)}$$

Gay-Lussac's (or Charles' Law)

This states that the volume of a given mass of a gas at constant pressure is directly proportional to the absolute temperature.

$$V \propto T \tag{2.2}$$

or $$\frac{V}{T} = \text{constant (at constant } p \text{ and mass)}$$

Avogadro's Law

According to this law, equal volumes of all gases, under similar conditions of temperature and pressure, contain equal number (N) of molecules.

$$V \propto N \text{ (at constant } T \text{ and } p)$$

But the number of moles, $n = \dfrac{N}{N_a}$ where N_a represents Avogadro's number. (2.3)

$$\therefore \quad V \propto n$$

Dalton's Law of Partial Pressures

According to this law, the total pressure exerted by a mixture of two or more non-reacting gases in a definite volume, at any given temperature, is equal to the sum of the partial pressures which each gas would exert if it occupied the same volume alone, at the same temperature.

$$p = p_1 + p_2 + \cdots \tag{2.4}$$

where p is the total pressure and $p_1, p_2, \ldots$ are the partial pressures of different gases in the mixture.

Graham's Law of Effusion

This law states that, at constant temperature and pressure, the rates of effusion of various gases vary inversely as the square roots of their densities or molar masses.

$$\text{Rate of effusion} \propto \sqrt{\frac{1}{\rho}} \propto \sqrt{\frac{1}{M}} \qquad (\rho \propto M)$$

For two gases of density ρ_1 and ρ_2 (or molar masses M_1 and M_2) which effuse at rates r_1 and r_2, respectively,

$$\frac{r_1}{r_2} = \sqrt{\frac{\rho_2}{\rho_1}} = \sqrt{\frac{M_2}{M_1}} \tag{2.5}$$

EXAMPLE 2.1 (SI units) A certain mass of an ideal gas has a volume of 5 m³ at a pressure of 1.01×10^5 N m^{-2}. Calculate the pressure required to compress it to a volume of 0.5 dm³ at the same temperature.

Solution At constant temperature,

$$pV = \text{constant or } p_1V_1 = p_2V_2$$

$$p_1 = 1.01 \times 10^5 \text{ N m}^{-2}, \qquad V_1 = 5 \text{ m}^3 = 5 \times 10^3 \text{ dm}^3, \qquad V_2 = 0.5 \text{ dm}^3$$

$$p_2 = \frac{p_1V_1}{V_2} = \frac{(1.01 \times 10^5 \text{ N m}^{-2}) \times (5 \times 10^3 \text{ dm}^3)}{0.5 \text{ dm}^3}$$

$$= 1.01 \times 10^9 \text{ N m}^{-2}$$

EXAMPLE 2.2 A sample of gas occupies 300 dm³ at 27°C and 750 torr pressure.

(a) Calculate the contraction in volume when the gas is cooled to −33°C at 750 torr pressure.

(b) Calculate the change in volume when the pressure is reduced by 150 torr at the same temperature.

Solution (a) At constant pressure:

$$\frac{V}{T} = \text{constant} \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 300\ \text{dm}^3, \qquad T_1 = 273 + 27 = 300\ \text{K},$$
$$T_2 = 273 - 33 = 240\ \text{K}$$
$$V_2 = \frac{V_1}{T_1} \times T_2 = \frac{300\ \text{dm}^3 \times (240\ \text{K})}{300\ \text{K}}$$
$$= 240\ \text{dm}^3$$

Thus, contraction in volume $= 300 - 240 = 60\ \text{dm}^3$.

(b) Since temperature is constant,

$$pV = \text{constant or } p_1V_1 = p_2V_2$$
$$p_1 = 750\ \text{torr}, \qquad V_1 = 300\ \text{dm}^3,$$
$$p_2 = 750 - 150 = 600\ \text{torr}$$
$$V_2 = \frac{p_1V_1}{p_2} = \frac{(750\ \text{torr}) \times (300\ \text{dm}^3)}{(600\ \text{torr})}$$
$$= 375\ \text{dm}^3$$

Thus, change in volume $= 375 - 300 = 75\ \text{dm}^3$.

EXAMPLE 2.3 (SI units) A perfectly elastic spherical balloon of 0.2 m diameter was filled with hydrogen at sea level, and released. What will be its diameter when it has risen to an altitude where the pressure is 65.6 kPa ? (Assume no change in temperature. Atmospheric pressure at sea level is 101.3 kPa).

Solution The volume V of a spherical balloon of radius r is given by

$$V = \frac{4}{3}\pi r^3$$

At sea level, volume $V_1 = \frac{4}{3}\pi r_1^3$

$r_1 = 0.2/2 = 0.1$ m $\quad V_1 = \frac{4}{3}\pi (0.1)^3$

Pressure at sea level, $p_1 = 101.3\ \text{kPa} = 101.3 \times 10^3\ \text{Pa}$

Volume at the altitude, $V_2 = \frac{4}{3}\pi r_2^3$

Pressure at the altitude, $p_2 = 65.6\ \text{kPa} = 65.6 \times 10^3\ \text{Pa}$

According to Boyle's law (temperature constant), (2.6)

$$p_1V_1 = p_2V_2$$

or
$$V_2 = \frac{p_1\,V_1}{p_2}$$

or
$$\frac{4}{3}\pi r_2^3 = \frac{(101.3 \times 10^3\ \text{Pa}) \times \frac{4}{3}\pi \times (0.1\ \text{m})^3}{65.6 \times 10^3\ \text{Pa}}$$

or
$$r_2^3 = \frac{101.3 \times (0.1)^3}{65.6}\ \text{m}^3$$
$$= 1.544 \times 10^{-3}\ \text{m}^3$$

or
$$r_2 = (1.544 \times 10^{-3})^{\frac{1}{3}}$$
$$= 0.1156\ \text{m}$$

Thus, diameter of the balloon at the altitude $= 0.1156 \times 2 = 0.2312$ m.

EXAMPLE 2.4 (SI units) Twenty-five dm³ of sulphur dioxide effuse through a porous partition in 75 s. What volume of oxygen will effuse in 90 s under similar conditions ? Molar masses of SO_2 and O_2 are 0.064 kg mol^{-1} and 0.032 kg mol^{-1}, respectively.

Solution According to Graham's law of effusion,

$$r \propto \sqrt{\frac{1}{M}}$$

or

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

Volume of sulphur dioxide $= 25$ dm³

Time taken $= 75$ s

Rate of effusion, $r_1 = \frac{25}{75}$ dm³ s^{-1}

Let volume of oxygen $= V$

Time taken $= 90$ s

Rate of effusion of O_2, $r_2 = \frac{V}{90}$ dm³ s^{-1}

Molar mass of SO_2, $M_1 = 0.064$ kg mol^{-1}

Molar mass of O_2, $M_2 = 0.032$ kg mol^{-1}

$$\frac{25/75}{V/90} = \sqrt{\frac{0.032}{0.064}}$$

$$\frac{25}{75} \times \frac{90}{V} = \sqrt{\frac{0.032}{0.064}}$$

or

$$V = \frac{25 \times 90}{75} \times \sqrt{2}$$

$$= 30 \times 1.414$$

$$= 42.42 \text{ dm}^3.$$

2.2 EQUATION OF STATE

The first three gas laws can be combined together to give the equation of state. This gives a quantitative relation between pressure, volume, temperature and number of moles, and is written as:

$$pV = nRT \tag{2.7}$$

where R is called the *universal gas constant*. The value of R is the same for all gases, and depends on the units used for p, V and T. In terms of the variables involved, the units of R are

$$R = \frac{pV}{nT} = \frac{\text{(force/area) volume}}{\text{mol K}} = \text{force length K}^{-1}\text{ mol}^{-1}$$
$$= \text{energy K}^{-1}\text{ mol}^{-1}$$

The different values of R in terms of different units of pressure and volume are

0.08206 l atm K^{-1} mol^{-1}	(p in atm, V in l)
8.314×10^7 erg K^{-1} mol^{-1}	(p in dynes cm^{-2}, V in cm^3)
1.987 cal K^{-1} mol^{-1}	(p in cal cm^{-3}, V in cm^3)
(SI units) 8.314 J K^{-1} mol^{-1}	(p in N m^{-2} or Pa, V in m^3)

Equation (2.7) can also be written as

$$pV = Nk_b\,T \tag{2.8}$$

where $k_b = \frac{R}{N_a}$ is known as the Boltzmann constant, which is the gas constant per molecule.

Real gases obey Equation (2.7) only at low pressure and high temperature and the equation is called the *ideal gas equation* or *perfect gas equation*. To account for the behaviour of real gases, several modifications have been made in Equation (2.7).

2.3 STANDARD TEMPERATURE AND PRESSURE

The properties of a gas depend upon the temperature and pressure. Hence it is convenient to specify a particular temperature and pressure for comparison of different gases. The standard conditions of temperature are abbreviated as STP and are

Temperature = 0°C or 273.15 K
Pressure = 1 atm or 760 mm Hg or 760 torr
or 101325 Pa (SI units)

Pressure is still expressed in terms of atmosphere and torr for many scientific measurements.

2.4 MOLAR MASS OF AN IDEAL GAS

Molar mass (earlier known as molecular weight) of an ideal gas can be obtained by rearranging Equation (2.7) into the form

$$pV = nRT$$

or

$$p = \frac{nRT}{V}$$

$$= \frac{m/M\,RT}{V} = \frac{\rho RT}{M} \qquad \left(\frac{m}{V} = \rho\right)$$

or

$$M = \frac{\rho RT}{p} \tag{2.9}$$

In practice, the density of a gas is measured at different pressures and fixed temperature, and a graph is plotted between ρ/p and p. The intercept obtained by extrapolating to zero pressure is equal to M/RT, i.e.

$$\lim_{p\to 0} \frac{\rho}{p} = \frac{M}{RT}$$

From this, molar mass M is calculated as

$$M = RT\left(\frac{\rho}{p}\right)_{p=0}$$

Example 2.5 (SI units) Calculate the volume occupied by 2 mol of an ideal gas at $2.5 \times 10^5\ \mathrm{N\,m^{-2}}$ pressure and 300 K temperature.

Solution According to the ideal gas equation,

$$pV = nRT \quad \text{or} \quad V = \frac{nRT}{p}$$

$$n = 2\ \mathrm{mol}, \qquad T = 300\ \mathrm{K}, \qquad p = 2.5 \times 10^5\ \mathrm{N\,m^{-2}},$$

$$R = 8.314\ \mathrm{N\,m\,K^{-1}\,mol^{-1}}$$

$$V = \frac{(2\ \mathrm{mol}) \times (8.314\ \mathrm{N\,m\,K^{-1}\,mol^{-1}}) \times (300\ \mathrm{K})}{(2.5 \times 10^5\ \mathrm{N\,m^{-2}})}$$

$$= 19.95 \times 10^{-3}\ \mathrm{m^3} \quad \text{or} \quad 19.95\ \mathrm{dm^3}$$

Example 2.6 (SI units) The density of air at 298 K and 101.325 kPa is $1.161\ \mathrm{kg\,m^{-3}}$. Assuming that air behaves as an ideal gas, calculate the average molar mass of air.

Solution Molar mass, $M = \dfrac{\rho RT}{p}$

$$\rho = 1.161\ \mathrm{kg\,m^{-3}}, \qquad T = 298\ \mathrm{K}, \qquad p = 101.325,$$

$$\mathrm{kPa} = 101.325 \times 10^3\ \mathrm{Pa}$$

$$R = 8.314\ \mathrm{N\,m\,K^{-1}\,mol^{-1}}$$

$$M = \frac{(1.161\ \mathrm{kg\,m^{-3}}) \times (8.314\ \mathrm{N\,m\,K^{-1}\,mol^{-1}}) \times (298\ \mathrm{K})}{(101.325 \times 10^3\ \mathrm{N\,m^{-2}})}$$

$$(1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}})$$

$$= 28.4 \times 10^{-3}\ \mathrm{kg\,mol^{-1}} = 28.4\ \mathrm{g\,mol^{-1}}$$

Note Molar mass (or molecular weight) of a substance is the mass in grams (CGS) or kilograms (SI) of one mole of the substance. Thus, in SI units molar mass is used in $\mathrm{kg\,mol^{-1}}$ instead of $\mathrm{g\,mol^{-1}}$ as used in CGS units. For example, molar mass of O_2 is $32 \times 10^{-3}\ \mathrm{kg\,mol^{-1}}$ (SI units) or $32\ \mathrm{g\,mol^{-1}}$ (CGS units).

Example 2.7 In a high-vacuum system, pressure as low as 10^{-8} mm Hg is desired. Calculate the number of molecules left per $\mathrm{cm^3}$, at 0°C in the system.

Solution Let us first calculate the number of moles left, using the ideal gas equation,

$$pV = nRT \quad \text{or} \quad n = \frac{pV}{RT}$$

$$p = 10^{-8}\text{ mm Hg} = \frac{10^{-8}}{760}\text{ atm},\ T^* = 273\text{ K},\ V = 1\text{ cm}^3$$
$$= 1\times10^{-3}\ l.$$

and
$$R = 0.082\ \text{l atm K}^{-1}\text{ mol}^{-1}$$
$$n = \frac{10^{-8}\times1\times10^{-3}}{760\times0.082\times273}\text{ mol cm}^{-3}$$

Now, number of molecules per cm³, $N = n \times N_a$

where $N_a = 6.022\times10^{23}$

$$N = \frac{10^{-8}\times1\times10^{-3}}{760\times0.082\times273}\times6.022\times10^{23}$$
$$= 3.54\times10^8\text{ molecules per cm}^3$$

2.5 KINETIC THEORY OF GASES

To account for the experimental observations (gas laws), a model was proposed known as the *kinetic theory of gases*. It was put forward by Bernoulli and was further developed and extended by Clausius, Krönig, Maxwell, Boltzmann and others. The main postulates of this theory are:

1. All gases consist of a very large number of minute particles called molecules.
2. Molecules are separated by large distances. Their volume is so small that it may be considered negligible in comparison to the total volume of the gas.
3. Molecules are constantly in rapid motion. During their motion, they collide with one another and also with the walls of the container.
4. Collisions of molecules with each other and with the walls of the container are perfectly elastic. However, there may be redistribution of energy during such collisions.
5. Pressure exerted by the gas on the walls of the container is due to the bombardment of gas molecules on the walls.
6. There is no interaction, attractive or repulsive, between molecules except at the time of collision.
7. **The average kinetic energy of molecules is directly proportional to the absolute temperature.**

2.6 KINETIC GAS EQUATION

From the postulates of the kinetic theory of gases, a mathematical expression can be derived known as the *kinetic gas equation*. Consider a certain gas made up of N molecules, each of mass m, enclosed in a cubical vessel of length L and volume V. Let us consider the motion of a particular molecule, moving with velocity v which can be resolved into three mutually perpendicular components v_x, v_y and v_z, so that

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*The actual value of 0°C is 273.15 K. However, for the sake of simplicity 273 has been used in calculations because it does not make a significant difference.

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

When a molecule moving along the x-axis with velocity v_x collides with the wall, it undergoes a change in momentum from mv_x to $-mv_x$ (collision is elastic). The change in momentum per collision is, therefore,

$$m\,v_x - (-m\,v_x) = 2\,m\,v_x$$

After the collision, the molecule takes l/v_x time to collide with the opposite wall, and it strikes the same face again in $2\,l/v_x$ time. Thus, the frequency of collisions with one face is $v_x/2\,l$, and the change in momentum per unit time is

$$2\,m\,v_x \times \frac{v_x}{2\,l} \quad \text{or} \quad \frac{m\,v_x^2}{l}$$

The force exerted by a molecule on the wall is equal to the change in momentum per unit time (Newton's law), i.e.

$$f = \frac{m\,v_x^2}{l}$$

For N molecules, the force will be

$$f = \sum_{i=1}^{N} \frac{m_i\,v_{xi}^2}{l}$$

if all the molecules are identical then $m_i = m$ and equation becomes

$$= \frac{m}{l}\sum_{i=1}^{N} v_{xi}^2 = \frac{mN}{l}\,\Sigma\frac{v_{xi}^2}{N}$$

$$= \frac{m\,N\,\overline{v_x^2}}{l}$$

where $\overline{v_x^2}$ is the average value of v_x^2 for the N molecules of the gas. (The average value is used because all the molecules are not moving with the same velocity.)

Now, pressure on the wall is equal to force per unit area. If area of wall is l^2, then pressure exerted is

$$p = \frac{mN}{l.l^2}\,\overline{v_x^2} = \frac{mN}{V}\,\overline{v_x^2} \qquad (l^3 = V)$$

But molecules in the gas are moving in all directions with equal probability. Hence,

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\left(\overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}\right) = \frac{1}{3}\,\overline{v^2}$$

Therefore,

$$p = \frac{1}{3}\,\frac{mN\,\overline{v^2}}{V}$$

or

$$pV = \frac{1}{3}\,mN\,\overline{v^2}$$

But mean square velocity $(\overline{v^2})$ is equal to the mean square speed $(\overline{c^2})$ Thus,

$$pV = \frac{1}{3}\, m N\overline{c^2}$$

This is called the *kinetic gas equation.* All the gas laws can be deduced from this equation.

2.7 KINETIC ENERGY AND TEMPERATURE

The average kinetic energy per molecule $\overline{\epsilon_k}$ is defined as

$$\overline{\epsilon_k} = \frac{1}{2}\, m\overline{c^2}$$

so that

$$pV = \frac{1}{3}\, mNc^2 = \frac{2}{3}\, N\overline{\epsilon_k} = \frac{2}{3}\, nN_a\overline{\epsilon_k}$$

where $N = nN_a$

But $N_a\overline{\epsilon_k}$ is the total kinetic energy per mole of gas, E_k, and $pV = nRT$, so that

$$pV = \frac{2}{3}\, nE_k \tag{2.10}$$

or $\frac{2}{3}\, nE_k = nRT$

or $E_k = \frac{3}{2}\, RT$ (for one mole of gas) (2.11)

The average kinetic energy per molecule is obtained by dividing both sides by Avogadro's number N_a:

$$\overline{\epsilon_k} = \frac{3}{2}\, k_bT$$

where $\frac{R}{N_a} = k_b$

Example 2.8 Derive Boyle's law, Charles' law and Avogadro's law from the kinetic gas equation,

$$pV = \frac{1}{3}\, mN\overline{c^2}.$$

Solution (*i*) *Boyle's law* According, to the kinetic gas equation

$$pV = \frac{1}{3}\, mN\overline{c^2} \tag{1}$$

According to one of the postulates of the kinetic theory of gases,

Average kinetic energy $\propto T$

i.e., $\frac{1}{2}\, m\overline{c^2} \propto T$ or $\frac{1}{2}\, m\overline{c^2} = K'T$ (2)

where K' is the proportionality constant

Introducing Eq. (2) in Eq. (1), we have

$$pV = \frac{1}{3} mN\overline{c^2} = \frac{2}{3} NK'T$$

Now, if temperature is constant, for a given mass of a gas (number of molecules N remain constant),

$$pV = \text{constant}$$

or $$p \propto \frac{1}{V}$$

This is the expression for Boyle's law.

(ii) *Charle's law.* It has been shown that

$$pV = \frac{2}{3} NK'T$$

or $$V = \frac{2}{3} \frac{NK'T}{p}$$

Now, if p is constant, for a given mass of a gas (i.e., N is constant), we have

$$V = \text{constant} \times T$$

or $$V \propto T$$

This is the expression for Charles' law.

(iii) *Avogadro's law* Let us consider two gases A and B. For these gases,

$$p_1V_1 = \frac{1}{3} m_1N_1\overline{c_1^2}$$

or $$p_1V_1 = \frac{2}{3} \times N_1K'T_1$$

$$p_2V_2 = \frac{1}{3} m_2N_2\overline{c_2^2}$$

or $$p_2V_2 = \frac{2}{3} \times N_2K'T_2$$

If we consider similar conditions of temperature and pressure,

$p_1 = p_2$ and $T_1 = T_2$, we have

$$\frac{V_1}{V_2} = \frac{N_1}{N_2}$$

Now, if volumes are equal, $N_1 = N_2$

Thus, equal volumes of all gases, under similar conditions of temperature and pressure, contain equal number of molecules. This is Avogadro's law.

EXAMPLE 2.9 (SI units) Calculate the pressure exerted by 2×10^{21} gaseous molecules of nitrogen in a container of 1 dm³ volume. The root mean square speed of molecules is 4.94×10^2 m s⁻¹.

Solution According to the kinetic gas equation,

$$pV = \frac{1}{3} mN\overline{c^2}$$

$N = 2 \times 10^{21}$ molecules, $V = 1\ dm^3 = 1 \times 10^{-3}$ m³,

$c = 4.94 \times 10^2$ m s^{-1}

Mass of nitrogen molecule,

$$m = \frac{28.0 \times 10^{-3}}{6.022 \times 10^{23}} = 4.65 \times 10^{-26} \text{ kg}$$

$$p = \frac{1}{3} \times \frac{(4.65 \times 10^{-26} \text{ kg}) \times 2 \times 10^{21} \times (4.94 \times 10^{2} \text{m s}^{-1})^2}{1 \times 10^{-3} \text{m}^3}$$

$$= 7.57 \times 10^3 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$= 7.57 \times 10^3 \text{ Pa (Pa} = \text{kg m}^{-1} \text{ s}^{-2})$$

EXAMPLE 2.10 Calculate the translational kinetic energy of 2 g of oxygen at −23°C in (i) ergs and (ii) calories.

Solution Translational kinetic energy,

$$E_k = \frac{3}{2} nRT$$

$$n = \frac{2}{32} \text{ mol}, \quad T = 273 - 23 = 250 \text{ K}$$

(i) $R = 8.314 \times 10^7 \text{ erg mol}^{-1}\text{K}^{-1}$

$$E_k = \frac{3}{2} \times \left(\frac{2}{32} \text{ mol} \right) \times (8.314 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1}) \times (250 \text{ K})$$

$$= 1.95 \times 10^9 \text{ ergs}$$

(ii) $R = 1.987 \text{ cal mol}^{-1} \text{ K}^{-1}$

$$E_k = \frac{3}{2} \times \left(\frac{2}{32} \text{ mol} \right) \times (1.987 \text{ cal mol}^{-1} \text{ K}^{-1}) \times (250 \text{ K})$$

$$= 46.57 \text{ cal.}$$

2 8 DISTRIBUTION OF MOLECULAR SPEEDS

All molecules present in a given sample of a gas do not possess the same speed. Their speeds are distributed over a wide range. This is because the molecules keep colliding with each other and their speeds keep changing. Maxwell has shown that the fraction of molecules having speed between c and $c + dc$ is expressed as

$$\frac{N_c}{N} = f(c)\, dc = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} c^2 \, e^{-Mc^2/2RT} \, dc \qquad (2.12)$$

$$= 4\pi \left(\frac{m}{2\pi k_b T} \right)^{3/2} c^2 \, e^{-mc^2/2k_bT} \, dc \qquad (2.13)$$

where N is the total number of molecules and N_c is the number of molecules having speed between c and $c + dc$.

The plots of Maxwell distribution of speeds show that the fraction of molecules with very high and very low speeds are very small. However, the biggest fraction of molecules possess the speed corresponding to the maximum in the distribution curve (Fig. 2.1). The speed possessed by the biggest fraction of molecules at a given temperature is called the

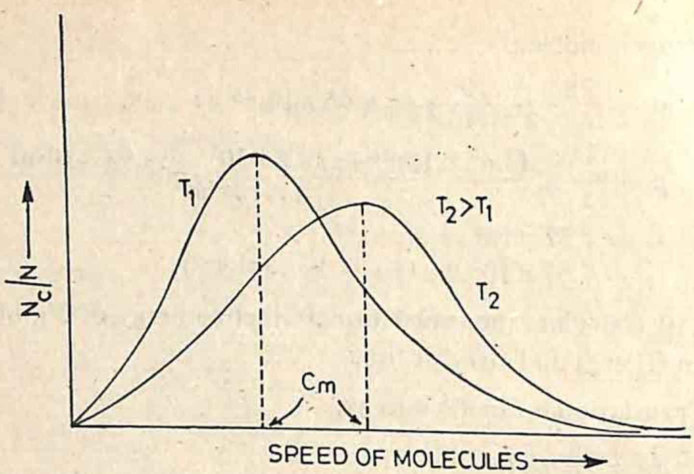

Fig. 2.1 *Maxwell distribution of speeds at temperature T_1 and T_2. The most probable speed, c_m, shifts to a higher value at the higher temperature, T_2.*

most probable speed (c_m). The magnitude of c_m increases with increase in temperature.

The *average speed* ($\bar{c}$) defined as the arithmetic mean of the different speeds of all the molecules present in a given sample of the gas. It is always positive number and should not be confused with the average velocity, which is zero due to random motion.

The *root mean square speed* (c) is the square root of the mean of the squares of different speeds of all the molecules.

If $c_1, c_2, c_3, \ldots, c_n$ represent the individual speeds of N molecules in a gas, then

$$\bar{c} = \frac{c_1 + c_2 + c_3 \ldots c_n}{N}$$

and

$$c = \left(\frac{c_1^2 + c_2^2 + c_3^2 + \ldots\ c_n^2}{N} \right)^{\frac{1}{2}}$$

These may be calculated from Maxwell distribution of speeds. We obtain the expressions

$$c_m = \sqrt{\frac{2RT}{M}}, \quad \bar{c} = \sqrt{\frac{8RT}{\pi M}} \quad \text{and } c = \sqrt{\frac{3RT}{M}}$$

$$c_m : \bar{c} : c = 1 : 1.128 : 1.224$$

The root mean square speed is commonly used and can be calculated from the relations:

$$c = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{\rho}} \qquad (2.14)$$

Note There is confusion in literature regarding the terms 'speed' and 'velocity' of gas molecules. As far as the root mean square velocity or root mean square speed are concerned, these two quantities are equivalent and either is acceptable. However, the average speed or most-probable speed are quite different from the mean velocity or most probable velocity. For example, the average velocity is always zero whereas the average speed is a definite positive number. For the sake of simplicity, we shall use the term speed throughout.

EXAMPLE 2.11 Calculate the value of $f(c)$ for oxygen molecules at 27°C for $c = c_m$.

Solution According to the Maxwell distribution of speeds,

$$f(c) = \frac{N_c}{Ndc} = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 e^{-Mc^2/2RT}$$

Here $c = c_m$

$$c_m = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2\times 8.314\times 10^7\times 300}{32}}$$

$$= 3.948\times 10^4 \text{ cm s}^{-1}$$

$$\left(\frac{M}{2\pi RT}\right)^{3/2} = \left(\frac{32}{2\times 3.14\times 8.314\times 10^7\times 300}\right)^{3/2}$$

$$= 2.92\times 10^{-15} \text{ cm}^{-3}\text{ s}^2$$

$$\frac{Mc^2}{2RT} = \frac{32\times (3.948\times 10^4)^2}{2\times 8.314\times 10^7\times 300} = 0.999$$

and $e^{-0.999} = 0.3679$

Thus,

$$f(c) = 4\times 3.14\times (2.92\times 10^{-15})\times (3.948\times 10^4)^2\times 0.3679$$

$$= 2.10\times 10^{-5} \text{ cm}^{-1}\text{ s}$$

EXAMPLE 2.12 (SI units) Calculate the root mean square speed of N_2 (molar mass = 0.028 kg mol^{-1}) at 298 K.

Solution Root mean square speed c is

$$c = \sqrt{\frac{3RT}{M}}$$

Here $M = 0.028$ kg mol^{-1}, $T = 298$ K, $R = 8.314$ J K^{-1} mol^{-1}

$$c = \sqrt{\frac{3\times 8.314\times 298}{0.028}} = 515.2 \text{ m s}^{-1}$$

EXAMPLE 2.13 The density of oxygen at 273 K and 1.01×10^5 N m^{-2} pressure is 1.42 kg m^{-3}. Calculate the root mean square, average and most probable speed of the oxygen molecules under these conditions.

Solution Root mean square speed

$$c = \sqrt{\frac{3pV}{M}} = \sqrt{\frac{3p}{\rho}}$$

$$\rho = 1.42 \text{ kg m}^{-3},\ p = 1.01\times 10^5 \text{ N m}^{-2}$$

$$c = \left[\frac{3\times 1.01\times 10^5}{1.42}\right]^{\frac{1}{2}} = 461.9 \text{ m s}^{-1}$$

Average molecular speed

$$\bar{c} = \sqrt{\frac{8pV}{\pi M}} = \sqrt{\frac{8p}{\pi\rho}} = \sqrt{\frac{8\times 1.01\times 10^5}{3.14\times 1.42}}$$

$$= 425.7 \text{ m s}^{-1}$$

Most probable speed,

$$c_m = \sqrt{\frac{2pV}{M}} = \sqrt{\frac{2p}{\rho}} = \sqrt{\frac{2\times 1.01\times 10^5}{1.42}}$$
$$= 377.2 \text{ m s}^{-1}$$

2.9 COLLISION FREQUENCY AND MEAN FREE PATH

The total number of collisions taking place in a unit volume per second is called the collision frequency. If there are N' molecules per unit volume $\left(\text{i.e. } N' = \frac{N}{V}\right)$ with molecular diameter d, then the number of collisions made by a single molecule with other molecules per second (called collision number), is equal to $\pi d^2 \bar{c} N'$, where $\bar{c}$ is the average speed of molecules. It is assumed that all other molecules are frozen in their positions. To improve the relation, $\bar{c}$ should be replaced by $\bar{c}_r$, which is the relative average speed, so that the collision number

$$Z_1 = \pi d^2 \bar{c}_r N'$$

But it can be shown that $\bar{c}_r = \sqrt{2}\,\bar{c}$, so that

$$Z_1 = \sqrt{2}\,\pi d^2 \bar{c} N'$$

The total number of bimolecular collisions occurring per second per unit volume of the gas (called collision frequency) is

$$Z_{11} = \frac{1}{2} Z_1 \times N' = \frac{1}{\sqrt{2}} \pi d^2 \bar{c} N'^2 \tag{2.15}$$

Here, the factor ½ is introduced to ensure that the collisions between two molecules are counted only once.

If it is a mixture of two gases A and B, then collision frequency is

$$Z_{AB} = (d_A + d_B)^2 \left(\frac{\pi RT}{2\mu}\right)^{\frac{1}{2}} N'_A\, N'_B \tag{2.16}$$

where d_A and d_B are diameters, N'_A and N'_B are the number of molecules per cm^3 of the two gases A and B, respectively, and μ is the reduced mass;

$$\mu = \frac{M_A M_B}{(M_A + M_B)} \tag{2.17}$$

The *mean free path* is defined as the average distance travelled by a molecule between two successive collisions. It is denoted by λ:

$$\text{Mean free path} = \frac{\text{Average distance travelled per second}}{\text{Number of collisions by a molecule per second}}$$

$$\lambda = \frac{\bar{c}}{Z_1} = \frac{\bar{c}}{\sqrt{2}\,\pi d^2 \bar{c} N'} = \frac{1}{\sqrt{2}\,\pi d^2 N'} \tag{2.18}$$

Effect of Temperature and Pressure on λ and Z

It can be shown that, for bimolecular collisions,

collision frequency $Z \propto \dfrac{p^2}{T^{\frac{3}{2}}}$

i.e. $Z \propto p^2$ provided T is constant

$Z \propto \dfrac{1}{T^{\frac{3}{2}}}$ provided p is constant

Similarly, mean free path, $\lambda \propto \dfrac{T}{p}$

i.e. $\lambda \propto \dfrac{1}{p}$ provided T is constant

$\lambda \propto T$ provided p is constant

EXAMPLE 2.14 The collision diameter of nitrogen is 3.74×10^{-8} cm. At 25°C and 760 torr, calculate

(a) the average number of collisions experienced by one molecule of nitrogen per second, and

(b) the average number of binary collisions of nitrogen gas per cm^3 per second.

Solution (a) The average number of collisions experienced by one molecule per second is given by

$$Z_1 = \sqrt{2}\,\pi d^2 \bar{c} N'$$

$$d = 3.74 \times 10^{-8} \text{ cm}$$

Number of molecules per cm^3, N' can be calculated as

$$N' = \frac{N}{V} = \frac{n \times N_a}{V} = \frac{p \times N_a}{RT} \qquad (pV = nRT)$$

$$p = \frac{760}{760} = 1 \text{ atm}, R = 0.082\ l \text{ atm. mol}^{-1}\text{ K}^{-1},$$

$$T = 298 \text{ K}$$

and $N' = \dfrac{1 \times 6.022 \times 10^{23}}{298 \times 0.082} = 2.464 \times 10^{22}$ molecules per litre

No. of molecules per cm^3 $= \dfrac{2.464 \times 10^{22}}{10^3} = 2.464 \times 10^{19}$ molecules per cm^3

Average speed of N_2 molecules at 25°C, $\bar{c}$, can be calculated as

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 10^7 \times 298}{3.14 \times 28}}$$

$$= 4.75 \times 10^4 \text{ cm s}^{-1}$$

Therefore, $Z_1 = 1.414 \times 3.14 \times (3.74 \times 10^{-8})^2 \times (4.75 \times 10^4) \times (2.464 \times 10^{19})$

$= 7.27 \times 10^9$ collisions per second.

(b) Average number of binary collisions per cubic centimetre per second.

$$Z_{11} = \frac{1}{\sqrt{2}} \pi d^2 \bar{c} (N')^2$$

$$= \frac{1}{1.414} \times 3.14 \times (3.74 \times 10^{-8})^2 \times (4.75 \times 10^4) \times (2.464 \times 10^{19})^2$$

$$= 8.96 \times 10^{28} \text{ collisions cm}^{-3} \text{ s}^{-1}$$

EXAMPLE 2.15 (SI units) Calculate the mean free path for oxygen molecule at 300 K and 101.325 kPa. The collision diameter of the oxygen molecule is 0.362 nm.

Solution The mean free path

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 N'}$$

$$d = 0.362 \text{ nm} = 3.62 \times 10^{-10} \text{ m}$$

Number of molecules in m^3 at 300 K

$$N' = \frac{p \times N_a}{R \times T}$$

where $p = 101325 \text{ N m}^{-2}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

$$N' = \frac{101325 \times 6.022 \times 10^{23}}{8.314 \times 300} = 2.45 \times 10^{25} \text{ molecules/m}^3$$

$$\therefore \quad \lambda = \frac{1}{1.414 \times 3.14 \times (3.62 \times 10^{-10})^2 \times (2.45 \times 10^{25})}$$

$$= 7.02 \times 10^{-8} \text{ m}$$

EXAMPLE 2.16 At what pressure will the mean free path of nitrogen molecule (diameter = 3.74×10^{-8} cm), at 27°C, be 1Å?

Solution Mean free path,

$$\lambda = \frac{1}{\sqrt{2} \pi d^2 N'}$$

Pressure can be calculated from the number of molecules per unit volume, N'.

$d = 3.74 \times 10^{-8}$ cm, $T = 273 + 27 = 300$ K and $\lambda = 1 \times 10^{-8}$ cm

$$\therefore \quad N' = \frac{1}{\sqrt{2} \pi d^2 \lambda}$$

$$= \frac{1}{1.414 \times 3.14 \times (3.74 \times 10^{-8})^2 \times 1.0 \times 10^{-8}}$$

$$= 1.61 \times 10^{22} \text{ molecules cm}^{-3}$$

Now, $$N' = \frac{p N_a}{RT}$$

or $$p = \frac{N' RT}{N_a}$$

$$= \frac{1.61 \times 10^{22} \times 0.082 \times 300}{6.022 \times 10^{23}}$$

$$= 0.658 \text{ atm}$$

2.10 HEAT CAPACITY OF GASES

The quantity of heat required to raise the temperature of a given body by one degree is called its *heat capacity*. For one mole of the substance, the heat capacity is called the *molar heat capacity*. The heat required depends on whether the pressure or volume is kept constant, when the temperature is raised by one degree. We define,

Heat capacity at constant volume $= C_V$ (volume kept constant but pressure increases)

Heat capacity at constant pressure $= C_p$ (pressure kept constant but volume increases)

The expansion of solids or liquids with temperature is quite small and hence their $C_V \approx C_p$. However, for gases, these are different. For one mole of an ideal gas

$$C_{p,m} - C_{V,m} = R \tag{2.19}$$

The ratio of two heat capacities is expressed by the symbol γ as

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} \tag{2.20}$$

For monoatomic gases, $\gamma = 1.66$ and its value decreases with increase in complexity of the gas molecule.

For polyatomic molecules, the heat supplied is used up not only in increasing the translational kinetic energy but also in increasing the vibrational and rotational energies. According to the *principle of equipartition of energy*, the total energy of a molecule is equally distributed among all types of motions or degrees of freedom.

It has been found that each translational degree of freedom contributes energy $\frac{1}{2}RT$ for one mole of a gas (or $\frac{1}{2}k_bT$ for one molecule). Monoatomic gases have only three translational degrees of freedom so that, for one mole of a monoatomic gas, the average kinetic energy is equal to $\frac{3}{2}RT$. Now, the heat capacity at constant volume is the change in internal energy with temperature at constant volume (refer Ch. 4). Therefore, $C_{V,m}$ for a monoatomic gas is,

$$C_{V,m} = \left(\frac{\partial U}{\partial T}\right)_V = \left[\frac{\partial(\frac{3}{2}RT)}{\partial T}\right] = \frac{3}{2}R \tag{2.21}$$

Polyatomic molecules, besides translational energy, also have rotational and vibrational energies. Each translational and rotational degree of freedom corresponds to $\frac{1}{2}RT$ per mole ($\frac{1}{2}kT$ per molecule) while each vibrational degree of freedom contributes RT per mole (kT per molecule) towards the total energy (because the vibrational mode has two terms; kinetic and potential energy). For a diatomic molecule there are three translational, two rotational and one vibrational degrees of freedom. Hence, for a mole of diatomic gas, the average internal energy is $3 \times \frac{1}{2}RT + 2 \times \frac{1}{2}RT + RT = \frac{7}{2}RT$. Thus $C_{V,m}$ is $\frac{7}{2}R$. For a polyatomic molecule having N atoms, there are three translational, three rotational and $(3N-6)$ vibrational degrees of freedom for non-linear and three translational, two rotational and $(3N-5)$ vibrational degrees of freedom for linear molecules. Thus, for non-linear molecules

$$U = \frac{3}{2} RT\,(\text{trans}) + \frac{3}{2} RT\,(\text{rot}) + (3N-6)\,R\,(\text{vib})$$

and $$C_{V,m} = \frac{3}{2} R + \frac{3}{2} R + (3N-6)\,R = (3N-3)\,R$$

for linear molecules

$$U = \frac{3}{2} RT\,(\text{trans}) + RT\,(\text{rot}) + (3N-5)\,R\,(\text{vib})$$

and $$C_{V,m} = \frac{3}{2} R + R + (3N-5)\,R = \left(3N - \frac{5}{2}\right) R$$

It has been found that for monoatomic gases, the heat capacities calculated from the equipartition principle agree well with the experimental values. However, for diatomic and polyatomic gases, the experimental values are lower than the values predicted from the equipartition principle. This is because vibrational degrees of freedom do not become active at lower temperatures.

EXAMPLE 2.17 Calculate the value of γ for the acetylene molecule using equipartition principle.

Solution Acetylene is a linear molecule. Hence,

$$C_{V,m} = \frac{3}{2} R + R + (3N-5)\,R$$

Here $N = 4$ so that

$$C_{V,m} = \frac{3}{2} R + R + (3 \times 4 - 5)\,R = \frac{19}{2} R$$

or $$C_{V,m} = \frac{19}{2} \times 1.987 = 18.877 \text{ cal.}$$

and $$C_{p,m} = C_{V,m} + R = 18.877 + 1.987$$
$$= 20.864 \text{ cal}$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{20.864}{18.877} = 1.11$$

2.11 VISCOSITY OF GASES

Like liquids, gases show viscous behaviour. *Viscosity* is the internal resistance that one part of a fluid offers to the flow of another part of the fluid. If the flow is considered as the movement of one layer over the other, then the force required for motion is

$$f = \eta A \left(\frac{dv}{dy}\right)$$

where η is the viscosity coefficient, dv is the difference in velocity of the two layers separated by distance dy, f is the force and A is the area of layers. The coefficient of viscosity can be calculated on the basis of the kinetic theory of gases by the relation,

$$\eta = \frac{m\bar{c}}{2\sqrt{2}\,\pi\, d^2} = \frac{(mk_bT)^{1/2}}{\pi^{3/2}\, d^2} \tag{2.22}$$

The viscosity is expressed in poise, *P* (*SI units* pascal second, Pa s). The viscosity of gases is determined by measuring the rate of flow through a very fine capillary. It is very useful for determining the diameter of gas molecules using Equation (2.22). The variation of *d* with pressure and temperature tells us about the nature of molecular interactions in the gas.

EXAMPLE 2.18 Calculate the coefficient of viscosity of CO_2 at 27°C using the kinetic theory of gases: *d* for CO_2 is 3.64×10^{-10} m.

Solution Coefficient of viscosity,

$$\eta = \frac{1}{\pi d^2}\left[\frac{mk_bT}{\pi}\right]^{\frac{1}{2}}$$

Here $T = 300$ K, $d = 3.64 \times 10^{-10}\ \text{m} = 3.64 \times 10^{-8}\ \text{cm}$,

$$k_b = \frac{8.314 \times 10^7 \text{erg/molecule K}}{6.022 \times 10^{23}} \quad \text{and}$$

$$m = \frac{44}{6.022 \times 10^{23}}\ \text{g}$$

$$\therefore \quad \eta = \frac{1}{3.14 \times (3.64 \times 10^{-8})^2\ \text{cm}^2}$$

$$\left[\frac{44\ \text{g}}{6.022 \times 10^{23}} \times \frac{8.314 \times 10^7\ \text{erg/molecule K}}{6.022 \times 10^{23}} \times \frac{300\ \text{K}}{3.14}\right]^{\frac{1}{2}}$$

$$= 2.37 \times 10^{-4}\ \text{g cm}^{-1}\ \text{s}^{-1} = 2.37 \times 10^{-4}\ \text{poise}$$

2.12 THERMAL CONDUCTIVITY OF GASES

The thermal conductivity of a gas is due to the transport of kinetic energy across a temperature gradient. The amount of thermal energy flowing per unit time is given by

$$Q \propto \frac{dT}{dZ}$$

where $\frac{dT}{dZ}$ is the temperature gradient along the *z*-axis.

or $$Q = \kappa\left(\frac{dT}{dZ}\right) \tag{2.23}$$

where κ (Kappa) is called the *coefficient of thermal conductivity*. The coefficient of thermal conductivity is the flow of thermal energy per unit time per unit area under unit temperature gradient. It has been shown to be given by

$$\kappa = \frac{1}{3}\bar{c}\,\lambda\, C_{V,m}\left(\frac{n}{V}\right) \qquad (2.24)$$

where λ is the mean free path, $\bar{c}$ is the average speed and $C_{V,m}$ is the molar heat capacity at constant volume,

or $$\kappa = \frac{1}{3}\,\bar{c}\, C_{V,m}\Big/\sqrt{2}\,\pi d^2 N_a \qquad (2.25)$$

Therefore, these relations can be used to calculate the mean free path, λ.

EXAMPLE 2.19 Calculate the thermal conductivity of argon at 27°C, given that the molar heat capacity at constant volume $= 12.5\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and collision diameter $= 5.6\times10^{-10}$ m.

Solution The thermal conductivity of argon

$$\kappa = \frac{1}{3}\,\bar{c}\, C_{V,m}\Big/\sqrt{2}\,\pi\, d^2 N_a$$

Here $$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$$

$$\kappa = \frac{1}{3}\left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} C_{V,m}\Big/\sqrt{2}\,\pi d^2 N_a$$

$$= \frac{2}{3}\left(\frac{RT}{M}\right)^{\frac{1}{2}} \frac{C_{V,m}}{\pi^{3/2}\, d^2 N_a}$$

$R = 8.314\ \mathrm{JK^{-1}mol^{-1}}$, $C_{V,m} = 12.5\ \mathrm{JK^{-1}\ mol^{-1}}$,

$M = 40\times10^{-3}\ \mathrm{kg\ mol^{-1}}$, $d = 5.60\times10^{-10}$ m

$$\kappa = \frac{2}{3}\left(\frac{8.314\times300}{40\times10^{-3}}\right)^{\frac{1}{2}}\times\frac{12.5}{(3.14)^{3/2}\,(5.6\times10^{-10})^2\times6.022\times10^{23}}$$

$$= 1.977\times10^{-3}\ \mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}.$$

MISCELLANEOUS EXAMPLES

EXAMPLE 2.20 The circulation of blood in the human body supplies oxygen and removes carbon dioxide. The concentration of oxygen and carbon dioxide is variable, but on the average 100 ml of blood contains 0.02 g of oxygen and 0.08 g of carbon dioxide. Calculate the volume of oxygen and carbon dioxide at 1 atm. and body temperature (37°C) assuming that there are 10 litres of blood in the human body.

Solution Volume of blood in human body $= 10\ l$

Weight of oxygen in blood $= \dfrac{0.02\times10\times1000}{100} = 2$ g

Weight of carbon dioxide in blood $= \dfrac{0.08\times10\times1000}{100} = 8$ g

To calculate volume, we use

$$pV = nRT \quad \text{or} \quad V = \frac{nRT}{p}$$

$p = 1$ atm, $\quad R = 0.082$ atm. l mol^{-1} K^{-1}, $\quad T = 273+37 = 310$ K

$$n \text{ for } O_2 = \frac{2}{32} \text{ mol}$$

$$V = \frac{2}{32} \times \frac{0.082 \times 310}{1} = 1.59 \text{ l}$$

$$n \text{ for } CO_2 = \frac{8}{44} \text{ mol}$$

$$V = \frac{8}{44} \times \frac{0.082 \times 310}{1} = 4.62 \text{ l}$$

EXAMPLE 2.21 The thermal power station at Bhatinda consumes 3000 tonnes of coal a day.

(a) Calculate the minimum volume of air used for burning the coal, if it is assumed to be pure carbon.

(b) If the coal contains 2% sulphur, calculate the number of moles of SO_2 per m^3 of air over Bhatinda. The area of Bhatinda is 16 km^2 and SO_2 is assumed to be evenly distributed over the entire area up to a height of 300 m.

(c) If the coal is mixed with 20% $CaCO_3$, how many tonnes of CO_2 will be produced?

Solution

(a) Carbon reacts with oxygen as

$$C + O_2 \longrightarrow CO_2$$

12 g of carbon reacts with 1 mol of oxygen. Let us calculate the volume of air needed to burn 12 g of carbon at 27°C.

Now, one mole of oxygen at N.T.P. occupies 22 4 litres. The volume of oxygen at 300 K is

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$V_1 = 22.4 \, l, \quad T_1 = 273 \text{ K}, \quad T_2 = 300 \text{ K}$$

$$V_2 = \frac{300 \times 22.4}{273}$$

$$= 24.62 \text{ l.}$$

Air contains 21% oxygen by volume

Volume of air required to burn 12 g of carbon at 27°C

$$= \frac{24.62 \times 100}{21}$$

$$= 117.24 \, l$$

12 g of carbon require 117.24 l air

Amount of coal consumed per day = 3000 tonnes = 3000×10^6 g

$$\therefore \quad 3000 \times 10^6 \text{ g of carbon require } \frac{117.24}{12} \times 3000 \times 10^6$$

$$= 2.931 \times 10^{10} \, l \text{ air}$$

(b) If coal contains 2% sulphur, then sulphur present in 3000×10^6 g of coal is

$$\frac{3000\times10^6\times2}{100}=60\times10^6 \text{ g}$$

$$S+O_2\longrightarrow SO_2$$

32 g of sulphur will give 64 g SO_2

$\therefore$ 60×10^6 g of sulphur will give $=\frac{64}{32}\times60\times10^6$

$= 120\times10^6$ g SO_2

Moles of SO_2 produced $=\frac{120\times10^6}{64}$

$= 1.875\times10^6$ mol

Volume of atmosphere over Bhatinda $= 16\times10^6\times300$

$= 48\times10^8$ m^3

Moles of SO_2 per m^3 of air $=\frac{1.875\times10^6}{48\times10^8}$

$= 3.9\times10^{-4}$

(c) If coal is mixed with 20% $CaCO_3$,

$$CaCO_3\rightarrow CaO+CO_2$$
$$C+O_2\rightarrow CO_2$$

Then, $CaCO_3$ in 3000 tonnes of coal $=\frac{3000\times10^6\times20}{100}=600\times10^6$ g

and carbon $= 2400\times10^6$ g

CO_2 obtained from $CaCO_3=\frac{44}{100}\times600\times10^6$

$= 264\times10^6$ g

CO_2 obtained from carbon $=\frac{44}{12}\times2400\times10^6$

$= 8800\times10^6$

Total CO_2 produced $= (8800\times10^6+264\times10^6) = 9064\times10^6$ g

$= 9064$ tonnes

EXAMPLE 2.22 A person inhales about 400 ml of air (79% N_2 and 21% O_2 by volume) in each breath. Calculate the total number of molecules in each breath if the temperature of air is 27°C and the atmospheric pressure is 760 torr. Find the change in number of oxygen molecules in each breath if the person moves to a hill station where the temperature is 7°C and pressure 700 torr.

Solution 400 ml of air at 300 K and 760 torr pressure contain

$$\frac{400\times79}{100}=316 \text{ ml of } N_2$$

$$\frac{400\times21}{100}=84 \text{ ml of } O_2$$

Moles of N_2 in each breath

$$n = \frac{pV}{RT}$$

where $p = \frac{760}{760} = 1$ atm, $T = 300$ K, $V = 316$ ml,

$$R = 82.0 \text{ atm ml K}^{-1} \text{ mol}^{-1}$$

$$= \frac{1 \times 316}{82.0 \times 300}$$

$$= 0.0128 \text{ mol}$$

Number of molecules of $N_2 = 0.0128 \times 6.022 \times 10^{23} = 7.74 \times 10^{21}$

Moles of O_2 in each breath

$$n = \frac{1 \times 84}{82.0 \times 300} = 0.00341 \text{ mol}$$

Number of molecules of $O_2 = 2.06 \times 10^{21}$

Total number of molecules in each breath $= (7.74 + 2.06) \times 10^{21}$

$= 9.80 \times 10^{21}$

If the person moves to a hill station where $p = 700$ torr,

$$= \frac{700}{760} \text{ atm, and } T = 273 + 7 = 280 \text{ K,}$$

$$\text{Moles of } O_2 = \frac{700 \times 84}{760 \times 82.0 \times 280}$$

$$= 0.00337 \text{ mol}$$

Number of molecules $= 0.00337 \times 6.022 \times 10^{23} = 2.03 \times 10^{21}$

Decrease in molecules of $O_2 = (2.06 - 2.03) \times 10^{21}$

$= 0.03 \times 10^{21} = 3 \times 10^{19}$

EXAMPLE 2.23 A balloon weighing 50 kg has a radius of 10 m. What will be its pay load if it is filled with He at 1 atm and 25°C? How will the pay load be affected if He is replaced by H_2?

(Density of air $= 1.22 \text{ kg m}^{-3}$)

Solution

Volume of balloon, $V = \frac{4}{3} \pi r^3$

Here $r = 10$ m $\therefore V = \frac{4}{3} \times 3.14 \times (10)^3$

$= 4.187 \times 10^3 \text{ m}^3$

Mass of displaced air $= 4.187 \times 10^3 \text{ m}^3 \times 1.22 \text{ kg m}^{-3}$

$= 5108$ kg

Moles of gas present in $V = 4187 \text{ m}^3$, $p = 1$ atm, $T = 298$ K

$$n = \frac{pV}{RT} = \frac{1 \times 4187 \times 10^3}{0.082 \times 298} \text{ mol}$$

$$= 171.3 \times 10^3 \text{ mol}$$

If the balloon is filled with helium,

Mass of helium = $171.3 \times 10^3 \times 4$

$= 685.2 \times 10^3$ g = 685.2 kg

Mass of balloon + helium gas = $685.2 + 50 = 735.2$ kg

Pay load = Mass of displaced air − Total mass of balloon

$= 5108 - 735.2$

$= 4372.8$ kg

If the balloon is filled with hydrogen,

Mass of H_2 = $171.3 \times 10^3 \times 2$

$= 342.6$ kg

Mass of balloon + H_2 gas = $50 + 342.6 = 392.6$ kg

Pay load = $5108 - 392.6$

$= 4715.4$ kg

EXAMPLE 2.24 Derive an expression for the most probable speed from the Maxwell distribution function,

$$f(c) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} c^2 \, e^{-Mc^2/2RT}$$

Calculate the most probable speed of N_2 molecules at 27°C.

Solution For most probable speed, $\frac{df(c)}{dc} = 0$

Differentiating R.H.S. with respect to c and equating the result to zero, i.e.

$$4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \left[c^2 \, e^{-Mc^2/2RT} \left(\frac{-2Mc}{2RT}\right) + 2\,c\, e^{-Mc^2/2RT}\right] = 0$$

or $$e^{-Mc^2/2RT}\left[2c - \frac{Mc^3}{RT}\right] = 0$$

or $$\frac{Mc^3}{RT} = 2c$$

$$c^2 = \frac{2RT}{M}$$

or $$c = \sqrt{\frac{2RT}{M}}$$

Thus, most probable speed $c_m = \sqrt{\frac{2RT}{M}}$

For N_2,

$M = 28 \times 10^{-3}$ kg mol^{-1}, $T = 300$ K, $R = 8.314$ J mol^{-1} K^{-1}

$$c_m = \sqrt{\frac{2 \times 8.314 \times 300}{28 \times 10^{-3}}}$$

$= 422.09$ m s^{-1}

QUESTIONS

Numerical Problems

2.1 (SI units) An iron cylinder contains helium at a pressure of 250 kPa and 300 K. The cylinder can withstand a pressure of 10^6 Pa. The room in which the cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not (the melting point of cylinder is 1800 K).

2.2 (SI units) What amount of nitrogen is contained in 0.15 m^3 of gas at a pressure of 1.05×10^5 N m^{-2} and a temperature of 300 K (assuming ideal behaviour)?

2.3 A gas balloon of volume 10 dm^3 at 27°C and 760 torr pressure rises to an altitude where the temperature is -13°C and the pressure 500 torr. What is the volume of the balloon at this altitude?

2.4 A flask is filled with a gas to a pressure of 6 atm at 27°C. (a) What pressure will develop inside the sealed flask if it is heated to 127°C. (b) At what temperature would the pressure be 4 atm?

2.5 Carbon dioxide occupies 25 dm^3 at 760 torr and 27°C. Calculate the number of (a) moles and (b) molecules.

2.6 (SI units) The density of a certain gas is 5.46 kg m^{-3} at 298 K and 103.3×10^3 N m^{-2}. Calculate its molar mass.

2.7 The density of a gas is found to be 1.76/g l^{-1} at 30°C and 760 torr pressure. What is its density at STP?

2.8 (SI units) Calculate the value of the gas constant R in SI units when pressure is expressed in N m^{-2} and volume in m^3.

2.9 A sample of an ideal gas weighing 0.2086×10^{-3} kg occupies a volume of 0.4 dm^3 at 630 torr and 37°C. Calculate its molar mass.

2.10 (SI units) Calculate the pressure exerted on the walls of a 5 dm^3 flask when 1.4 g of N_2 is introduced into it at 300 K.

2.11 Three boxes A, B and C are of 1.5, 2.5 and 4.0 l capacity respectively. Box A contains 0.5 g of N_2 gas at a pressure of 740 torr, box B contains 1 g of argon gas at a pressure of 480 torr, and box C contains neon at 160 torr. What will be the pressure in box C if the contents of A and B are completely transferred to C (assume ideal behaviour). All the boxes are at the same temperature before and after transfer.

2.12 A boy breathes in 25 cm^3 of air at 760 torr pressure and 27°C. Calculate the number of molecules that enter the lungs of the boy.

2.13 A spherical balloon of 100 g has a radius of 30 cm. Calculate the moles of hydrogen present in the balloon when it will just rise. The density of air under these conditions is 1.29 g l^{-1}.

2.14 A spherical balloon of diameter 20 dm weighs 2 kg. What will be its pay load if it is filled with helium at 1 atm and 27°C? How will the pay load be affected if hydrogen is filled instead of helium? (Molar mass of air may be taken to be 28.9 g mol^{-1}).

2.15 (SI units) A perfectly elastic balloon is filled with helium and is expected to rise to a height of 30 km, at which point it will be fully inflated and have a volume of 100 m^3. The temperature at this height is 265 K and the atmospheric pressure 0.2 kPa. How many kilograms of helium will be needed to inflate the balloon fully.

2.16 (SI units) A discharge tube of 2 dm^3 capacity containing hydrogen gas was evacuated till the pressure inside was 0.1 N m^{-2}. If the tube was maintained at a temperature of 300 K, calculate the number of hydrogen molecules still present in the tube.

2.17 N_2O_4 molecules in a sample of gas are 20% dissociated to NO_2 at 27°C and 760 torr. Calculate the density of the equilibrium mixture at that temperature.

2.18 A certain mixture of helium and neon in a 5 *l* flask at 27°C and 1 atm weight 4 g. What is the composition of the mixture in weight per cent? What will be the partial pressure of helium and neon (atomic masses of He = 4, Ne = 20).

2.19 (SI units) Under the same conditions of temperature and pressure, oxygen effuses through a porous partition at the rate of 0.360 m^3 in 60 s and an unknown gas at the rate of 0.210 m^3 in 50 s. If the molar mass of oxygen is 0.0320 kg $mole^{-1}$, calculate the molar mass of the unknown gas.

2.20 A sample of ozonised oxygen contains 82.4% ozone by weight. It required 372 s to diffuse through a porous partition while pure oxygen required 319 s. Determine the vapour density of ozone.

2.21 A tube was filled with 500 g of an ideal gas (molar mass = 40 g mol^{-1}) at 27°C and 760 torr. After two days, due to leakage through the valve, a certain amount of gas escaped and the pressure fell to 600 torr at the same temperature. How much gas has leaked out?

2.22 Suppose a flask was filled with nitrogen molecules all having the same speed 4.9×10^4 cm s^{-1}. The molecules were allowed to collide with one another until a Maxwell distribution was established. Calculate the temperature at equilibrium (assume that no heat exchange occurs between the gas and its surroundings).

2.23 (SI units) The density of an unknown gas at 273 K and 1.05×10^5 N m^{-2} is 1.52 kg m^{-3}. Calculate the root mean square speed of the molecules of the gas under these conditions.

2.24 At what temperature will the root mean square speed of SO_2 be the same as that of O_2 at 27°C?

2.25 The root mean square speed of oxygen molecules at 760 torr and 0°C is 4.61×10^4 cm s^{-1}. Calculate the density of oxygen.

2.26 Calculate the total kinetic energy of 1.5 mole of an ideal gas at 27°C in (i) ergs (b) joules and (c) kcal.

2.27 By plotting the graph of ρ/p vs p, the limiting value of $\frac{\rho}{p}$ of carbon dioxide at 273 K has been found to be 0.01938 g J^{-1}. Calculate the molar mass of the gas.

2.28 The average molecular speed of CO_2 is 3.68×10^2 m s^{-1} at 273 K. What is its speed at 300 K?

2.29 A 2 *l* gas bulb contains 2.75×10^{20} molecules of O_2 exerting a pressure of 1 atm. Calculate the root mean square speed and temperature.

2.30 Calculate the average kinetic energy (in calories) of 2 g of sulphur dioxide at 27°C.

2.31 The collision diameter of an oxygen molecule is 3.62×10^{-8} cm. Calculate the number of binary collisions per cm^3 per second at 1 atm and 25°C.

2.32 Calculate and compare the mean free paths of H_2 ($d = 2.18$ Å) and He ($d = 2.73$ Å) at 1 atm and 27°C.

2.33 Calculate the values of λ, Z_1, Z_{11} for N_2 at 1 atm and 25°C, given van der Waals constant $b = 3.913 \times 10^{2}$ l mol^{-1}.

2.34 The mean free path of two gases A and B are in the ratio $\lambda_A/\lambda_B = 2.6$ at 27°C and 1 atm pressure. Calculate the ratio of their diameters d_A/d_B.

2.35 (SI units) Calculate temperatures at which the average speed of hydrogen becomes equal to (i) CH_4 and (ii) O_2 at 300 K.

2.36 (SI units) Calculate the average, the most probable and the root mean square speeds for oxygen molecules (molecular mass = 0.032 kg mol^{-1}) at 298 K.

2.37 The collision diameter of $O_2 = 3.61 \times 10^{-10}$ m. Calculate its coefficient of viscosity at 27°C from the kinetic theory of gases.

2.38 Calculate the value of the probability distribution $\frac{1}{N}\left(\frac{dN}{dc}\right)$ for nitrogen molecules at 27°C. The molecular speed $c = 2.12 \times 10^3$ m s^{-1}.

2.39 The coefficient of viscosity of N_2 gas is 1.78×10^{-4} poise. Calculate the mean free path at a pressure of 10^{-4} mm of Hg at 25°C.

2.40 Calculate the thermal conductivity of helium gas at 27°C given that $C_{V,m} = 12.5$ J K^{-1} mol^{-1} and collision diameter $= 2.07$ Å.

QUIZ QUESTIONS

Type A: Multiple Choice

2.41 For a given mass of a gas, if temperature increases
- (a) pressure and volume remain constant
- (b) volume increases provided pressure is constant
- (c) pressure decreases provided volume is constant
- (d) volume decreases provided pressure is constant

2.42 For a given mass of a gas at constant temperature, if the volume V becomes three times, then pressure p will become
- (a) $3\,p$
- (b) $p/3$
- (c) $3\,p/T$
- (d) $9\,p^2$

2.43 For a given mass of a gas, if pressure is reduced to half and temperature is doubled, then volume V will become
- (a) $4\,V$
- (b) $2\,V^2$
- (c) $V/4$
- (d) $8\,V$

2.44 Which of the following statements is not correct regarding the constant R in the ideal gas equation $pV = nRT$?
- (a) Its value is independent of temperature or pressure.
- (b) Its value is independent of the nature of gas.
- (c) It is called the universal gas constant per molecule.
- (d) In SI units its value is 8.314 J K^{-1} mol^{-1}.

2.45 The gases H_2, N_2, O_2 and NH_3 (molecular masses: $H_2 = 2$, $N_2 = 28$, $O_2 = 32$ and $NH_3 = 17$) will effuse in the order
- (a) $H_2 > N_2 > O_2 > NH_3$
- (b) $NH_3 > O_2 > N_2 > H_2$
- (c) $H_2 > N_2 > NH_3 > O_2$
- (d) $H_2 > NH_3 > N_2 > O_2$

2.46 Which of the following is not a correct postulate of the kinetic theory of gases?
- (a) The gas molecules are in random motion.
- (b) The gaseous collisions are perfectly elastic.
- (c) The average kinetic energies of different gases are equal at a particular temperature.
- (d) The pressure exerted on the walls of the container is due to the intermolecular forces.

2.47 The change in momentum when a molecule with mass m of an ideal gas moving with velocity v_x rebounds elastically, after hitting the wall, is
- (a) $2\,mv_x$
- (b) $-mv_x$
- (c) zero
- (d) mv_x

2.48 If the average velocity of a molecule travelling in the x-direction in a cube of length l is c cm s^{-1}, the number of collisions per second with the same side of the wall is

(a) $c \times l$ (b) c/l

(c) $c/2\,l$ (d) $c \times l/2$

2.49 In terms of density, the kinetic gas equation may be written as

(a) $pV = \frac{1}{3}\,\rho\overline{c^2}$

(b) $pV = \rho\overline{c^3}$

(c) $p = \frac{1}{3}\,\rho\overline{c^2}$

(d) $p = \frac{1 \times \rho}{3\,V} \times \overline{c^2}$

2.50 For a gas having N molecules per unit volume, moving with an average speed of c m s^{-1} and molecular diameter d m, the mean free path is

(a) $\sqrt{2}\,\pi\,d^2N$

(b) $\sqrt{2}\,\pi\,d^2\,\bar{c}N$

(c) $\frac{1}{\sqrt{2}}\,\pi\,d^2\,\bar{c}N$

(d) $\frac{1}{\sqrt{2}\,\pi\,d^2N}$

2.51 The diameter of molecule B is half that of molecule A. The ratio of mean free path (λ_A / λ_B) will be

(a) 1/2 (b) 1/4

(c) 4 (d) 2

2.52 Two separate bulbs are filled with ideal gases A and B, respectively. The density of gas A is three times that of gas B and the molecular weight of gas B is twice that of gas A. Calculate the ratio of the pressure of gas A to gas B if the two gases are at the same temperature.

(a) 3/2 (b) 2/3

(c) 6/1 (d) 1/6

2.53 If the mean free path of a gas at 760 torr is λ, what will be its value at 5 atm pressure ?

(a) $\lambda/5$ (b) 5λ

(c) $\frac{5}{760}\,\lambda$ (d) λ^2

2.54 The mean free path of a gas at 1 atm is λ cm and the number of collisions made by one molecule per second is z'. The average speed of the molecules will be

(a) $\frac{\lambda}{z'}$ cm s^{-1} (b) $\lambda z'$ cm s^{-1}

(c) $\frac{1}{\sqrt{2}}\,\frac{\lambda}{z'}$ cm s^{-1} (d) $\sqrt{\frac{\lambda}{z'}}$ cm s^{-1}

2.55 For a triatomic gas, $C_{p,m} - C_{V,m}$ is equal to

(a) $3\,R$ (b) R

(c) $3\,R$ (d) $(3-1)\,R$

2.56 If C_p is the heat capacity at constant pressure and C_V is the heat capacity at constant volume, then for noble gases C_p/C_V is

(a) 2.33 (b) 1
(c) 1.67 (d) 1.33

2.57 For triatomic linear molecules, $C_{V,m}$ may be expressed as

$$C_{V,m} = \frac{3}{2} R + R + (3N - 5) R$$

the molar heat capacity at constant pressure C_p will be equal to ($R \approx 2$ cal)

(a) 15 cal (b) 13 cal
(c) 11 cal (d) 12 cal

2.58 Which of the following statements is correct regarding the mean free path (λ) of a gas?

(a) $\lambda \propto T^{\frac{1}{2}}$ provided p is constant
(b) λ has no effect on T or p if the volume of the gas remains constant.
(c) $\lambda \propto p$ provided T is constant.
(d) $\lambda \propto \frac{1}{p}$ provided T and V are constant.

2.59 According to the kinetic molecular theory of gases, the average kinetic energy

(a) is proportional to temperature
(b) decreases with rise in temperature
(c) is always constant for a particular gas
(d) is zero at 0°C

2.60 For one mole of a gas, the total kinetic energy is equal to

(a) RT (b) $\frac{3}{2} RT$
(c) $\frac{2}{3} k_b T$ (d) $(C_p - C_v)/RT$

Type B: Multiple Choice (Numerical Problems)

2.61 If 360 dm³ of a gas were collected over water at 25°C and 720 torr, the volume of dry gas (aqueous tension of water at 25°C = 23.8 torr) at the same temperature and pressure is

(a) 348.10 dm³
(b) 174.05 dm³
(c) 34.81 dm³
(d) 696.20 dm³

2.62 At STP, 10 g of a gas occupies 2 l. At what temperature will the volume become double, at the same pressure and for the same quantity of gas?

(a) 273 K (b) −273°C
(c) 546 K (d) 546°C

2.63 Two samples of gases A and B are at the same temperature. The molecules of A are travelling four times faster than molecules of B. The ratio (m_A/m_B) of their masses will be

(a) 16 (b) 4
(c) 1/4 (d) 1/16

2.64 If 1000 ml of a gas A at 600 torr and 500 ml of gas B at 800 torr are placed in a 2 l flask, the final pressure will be

(a) 500 torr
(b) 1000 torr
(c) 850 torr
(d) 2000 torr

2.65 The number of molecules of an ideal gas in a 8.2 *l* container at 380 torr and 27°C will be
(a) 6.02×10^{23}
(b) 1.0×10^{23}
(c) 1.0×10^{22}
(d) 12.04×10^{23}

2.66 The relative rates of effusion of oxygen and hydrogen, at the same temperature and pressure, are in the ratio (molar masses of $H_2 = 2$ and $O_2 = 32$)
(a) 1 : 4 (b) 1 : 8
(c) 4 : 1 (d) 16 : 1

2.67 Two gases *X* and *Y*, having the same volume, effuse through an orifice in 30 and 10 min, respectively. The molar mass of *X* is 162. The molar mass of *Y* is
(a) 54 (b) 324
(c) 18 (d) 486

2.68 A box is divided into two equal compartments by a thin partition, and they are filled with gases *A* and *B*, respectively. The two compartments have a pressure of 200 torr each. The pressure after removing the partition will be equal to
(a) 400 torr (b) 100 torr
(c) 200 torr (d) 40,000 torr

2.69 Two separate bulbs contain ideal gases *A* and *B*, respectively. The density of gas *A* is twice that of gas *B* and the molar mass of gas *A* is half that of gas *B*. If the two gases are at the same temperature, the ratio of pressure of *A* to that of *B* is
(a) 1 (b) 1/4
(c) 4 (d) 1/2

2.70 The root mean square speed of CH_4 molecules will become double its value at STP when the temperature is
(a) 546 K (b) 819°C
(c) 546°C (d) 819 K

2.71 The total kinetic energy of sample of gas which contains 1.0×10^{22} molecules is 24×10^2 J at −123°C. Another sample of gas at 27°C has a total kinetic energy 48×10^2 J. The number of molecules in the second sample is
(a) 2×10^{22} (b) 1×10^{22}
(c) 1×10^{24} (d) 5×10^{21}

2.72 The root mean square speed of oxygen at 27°C is 800 cm s^{-1}. The root mean square speed of hydrogen at the same temperature will be
(a) 3200 cm s^{-1} (b) 200 cm s^{-1}
(c) 1600 cm s^{-1} (d) 400 cm s^{-1}

2.73 The temperature of a sample of SO_2 is raised from 27 to 327°C. The average kinetic energy of the gas molecules is
(a) doubled
(b) raised to the power two
(c) halved
(d) multiplied by a factor 327/27.

2.74 The root mean square speed of SO_2 gas becomes the same as that of oxygen at 27°C when the temperature is
(Atomic masses: S = 32, O = 16)
(a) 327°C (b) 127°C
(c) 54°C (d) 227°C

2.75 The mean free path of a certain gas at 27°C and 101325 N m^{-2} is 5.0×10^{-5} m, and the number of molecules with which it collides per m^3 per second is

4.0×10^{10}. The average speed of molecules is

(a) 1.25×10^{-15} m s^{-1}
(b) 0.8×10^{5} m s^{-1}
(c) 2×10^{6} m s^{-1}
(d) 2×10^{4} m s^{-1}

2.76 4.0 g of argon in a bulb at a temperature of T K had a pressure p. When the bulb was placed in a hotter bath at a temperature 50 more than the first one, 0.8 g of the gas had to be removed to get the original pressure p. The original temperature T is equal to. (Atomic mass of argon = 40)

(a) 510 K
(b) 200 K
(c) 73 K
(d) 100 K

2.77 The root mean square speed of gas molecules at 25 K and 1.5×10^{5} N m^{-2} is 100.5 m s^{-1}. If the temperature is raised to 100 K and the pressure to 6.0×10^{5} N m^{-2}, the root mean square speed becomes

(a) 201.0 m s^{-1}
(b) 100.5 m s^{-1}
(c) 402.0 m s^{-1}
(d) 1608.0 m s^{-1}

2.78 56 g of gaseous N_2 (molar mass = 28) are mixed with 44 g of CO_2 (molar mass = 44) and the pressure of the resulting mixture is 303.9 kPa. The partial pressure of N_2 in the mixture is

(a) 101.3 kPa
(b) 202.6 kPa
(c) 303.9 kPa
(d) 405.4 kPa

2.79 An electronic vacuum tube was sealed off, during an experiment, at a pressure of 8.2×10^{-10} atm at 27°C. The volume of the tube was 30 dm^3. Calculate the number of gas molecules remaining in the tube.

(a) 6.022×10^{14}
(b) $8.2 \times 6.022 \times 10^{23}$
(c) 24.6×10
(d) $8.2 \times 30 \times 6.022 \times 10^{23}$

2.80 The total kinetic energy of 2 mol of an ideal gas at 127°C, in kilojoules, is

(a) 8.31 kJ
(b) 24.94 kJ
(c) 7.48 kJ
(d) 9.98 kJ

Type C: True or False Statements

2.81 When the pressure of a gas is tripled (at constant temperature), the volume is reduced to one-third its original volume.

2.82 The product of pressure and volume of a fixed amount of a gas is independent of temperature.

2.83 Wet air will diffuse through a tiny hole faster than dry air.

2.84 The root mean square speed is always more than the average speed of molecules.

2.85 Molecules of different gases have the same average kinetic energy at a given temperature.

2.86 The thermal conductivity of a gas is due to the transport of kinetic energy across a temperature gradient.

2.87 The quantity of heat required to raise the temperature of 1 g of a substance by one degree is called heat capacity.

2.88 For solids, C_p is approximately equal to C_V.

2.89 A diatomic molecule has three translational, two rotational and one vibrational degrees of freedom.

2.90 According to the postulates of the kinetic theory, the forces of interaction between molecules are negligible only for ideal gases.

Type D: Fill in the Blanks

2.91 Collision frequency——————with the increase in temperature.

2.92 The number of molecules with which a single molecule collides per second is called——————.

2.93 Gases having molecules that do not attract one another and occupy virtually no volume are called——————gases.

2.94 The pressure-volume curves plotted at different fixed temperatures are called ——————.

2.95 Mean free path——————with increase in pressure of the gas at constant temperature.

2.96 The gas constant per molecule is called——————.

2.97 The molar heat capacity at constant pressure for one mole of a——————gas is 9/2 *R*.

2.98 The thermal conductivity of a gas is due to the transport of——————across a temperature gradient.

2.99 The quantity of heat required to raise the temperature by one degree of 1 g of a substance is called——————.

2.100 According to the kinetic molecular theory of gases, the average kinetic energy is proportional to——————.

ANSWERS

Numerical Problems

2.1 The pressure of the gas at the melting point of the cylinder is calculated as $p = 1.5 \times 10^6$ Pa. This is more than the pressure which the cylinder can withstand (1×10^6 Pa). Thus, it will blow up before it melts. *2.2* 0.177 kg *2.3* 13.16 dm^3 *2.4* (a) 8 atm. (b) −73°C *2.5* (a) 1.016 (b) 6.11×10^{23} *2.6* 130.9 *2.7* $\rho = \frac{Mp}{RT}$ and $\frac{\rho_2}{\rho_1} = \frac{p_2}{p_1} \times \frac{T_1}{T_2}$ therefore $\rho_2 = 2.12$ g/*l* *2.8* 8.314 J K^{-1} mol^{-1} *2.9* 16.0 *2.10* 24.94×10^3 N m^{-2} *2.11* 737.5 torr *2.12* 6.118×10^{20} *2.13* Volume of balloon $= \frac{4}{3} \pi r^3 = 113.04\ l$. When balloon just rises, weight of balloon *plus* contents = weight of 113.04 *l* air $= 113.04 \times 1.29 = 145.82$ g. Weight of hydrogen in balloon $= 145.82 - 100 = 45.82$ g. Moles of $H_2 = 22.91$ *2.14* Volume of balloon $= \frac{4}{3} \pi r^3 = 33.49 \times 10^3\ dm^3$, density of air $\rho = \frac{Mp}{RT} = 1.17\ g\ dm^{-3}$, mass of displaced air $= 33.49 \times 10^3 \times 1.17 = 39.18$ kg, moles of helium present in balloon at 1 atm and 27°C, $n = \frac{pV}{RT} = \frac{1 \times 33.49 \times 10^3}{0.082 \times 300} = 1.36 \times 10^3$, mass of helium in balloon $= 1.36 \times 10^3 \times 4 = 5.440$ kg, total mass of balloon $= 2.0 + 5.44 = 7.44$; Thus pay load $= 39.18 - 7.44 = 31.74$ kg. Similarly, if helium is replaced by hydrogen, pay load = 34.46 kg *2.15* 0.0363 kg *2.16* 4.83×10^{16} *2.17* Consider one mole of undissociated N_2O_4 in the beginning. When 20% N_2O_4 is dissociated, moles of N_2O_4 left = 0.80; moles of N_2O_4 formed = 0.40. Volume of total 1.20 mol at 300 K and 760 torr = 29.53 *l*, density = 92/29.53 = 3.12 g l^{-1} *2.18* Wt % He = 25.8, Wt % Ne = 74.2 *2.19* 5.95 kg mol^{-1} *2.20* 23.56 *2.21* 105.44 g *2.22* 269.7 K *2.23* 455.2 ms^{-1} *2.24* 327°C *2.25* 1.431×10^{-3} *2.26* (a) 5.61×10^{10} erg (b) 5.61×10^3 J (c) 1.342 kcal *2.27* 43.99 *2.28* 3.86×10^{12} ms^{-1} *2.29* $6.45 \times 10_4$ cm s^{-1} *2.30* 27.9 cal. *2.31* 3.18×10^{28} *2.32* $\lambda(He) = 1.23 \times 10^{-7}$ cm and $\lambda(H_2) = 1.93 \times 10^{-7}$ cm *2.33* $\lambda = 9.27 \times 10^{-6}$ cm, $Z_1 = 4.12 \times 10^9$ collisions s^{-1},

$Z_{11} = 6.30 \times 10^{28}$ collisions $cm^{-3}\,s^{-1}$ *2.34* 1 : 0.62 *2.35* (i) 37.5 (ii) 18.75 *2.36* 448 ms^{-1}, 392 ms^{-1}, 476 . ms^{-1} *2.37* 2.045×10^{-4} poise *2.38* 1.49×10^{-13} ms^{-1} *2.39* 49.7 cm *2.40* 1.45×10^{-3} $Jm^{-1}\,s^{-1}\,K^{-1}$

Quiz Questions

2.41 (b) *2.42* (b) *2.43* (a) *2.44* (d) *2.45* (d) *2.46* (d) *2.47* (a) *2.48* (c) *2.49* (c) *2.50* (d) *2.51* (b) *2.52* (c) *2.53* (a) *2.54* (b) *2.55* (b) *2.56* (c) *2.57* (a) *2.58* (b) *2.59* (a) *2.60* (b) *2.61* (a) Applying $p_1V_1 = p_2V_2$ (T is constant) final volume is 348.1 dm^3 *2.62* (c) *2.63* (d) *2.64* (a) *2.65* (b) *2.66* (a) *2.67* (c) *2.68* (c) *2.69* (c)

$p = \frac{\rho RT}{M}$; $\frac{p_A}{p_B}\ \frac{\rho_A/\rho_B}{M_A/M_B} = \frac{\rho_A}{\rho_B} \times \frac{M_B}{M_A} = 2 \times \frac{2}{1} = 4$ *2.70* (b) *2.71* (b) *2.72* (a)

2.73 (a) *2.74* (a) *2.75* (c) *2.76* (b) *2.77* (b) *2.78* (b) *2.79* (a) *2.80* (d) *2.81* True *2.82* False *2.83* True *2.84* True *2.85* True *2.86* True *2.87* False; It is called specific heat *2.88* True *2.89* False *2.90* True *2.91* increases *2.92* collision number *2.93* ideal *2.94* isotherms *2.95* increases *2.96* Boltzman constant *2.97* diatomic *2.98* kinetic energy *2.99* specific heat, molar heat capacity *2.100* temperature.

3

Real Gases and Critical Phenomena

Any gas conforming to the equation $pV = nRT$ at all temperatures and pressures is called an ideal gas. However, real gases do not obey this equation over the entire range of temperature and pressure. Many attempts have been made to study the deviations of real gases from ideal behaviour and a large number of equations of state have been proposed.

3.1 DEVIATIONS OF REAL GASES FROM IDEAL BEHAVIOUR

The deviations of real gases from ideal behaviour can be observed by plotting a graph between pV/nRT (called the *compressibility factor*, Z), and p (Fig. 3.1). For an ideal gas Z should be equal to one and

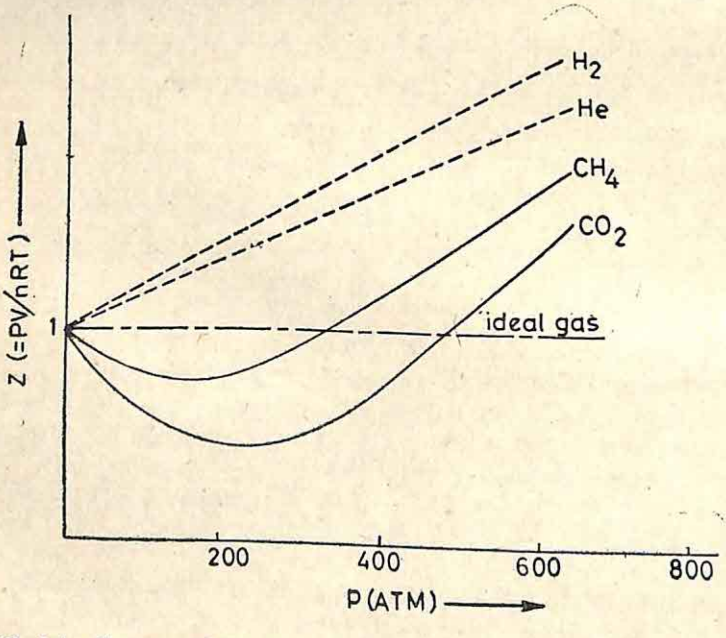

FIG. 3.1 *Compressibility factor, Z against p for some gases at 0°C.*

independent of temperature and pressure. However, it has been found that Z depends on both temperature and pressure. For example, at 0°C for H_2 and He, Z is always greater than one (shown dotted). For CH_4 and CO_2, Z is less than one at low pressures and greater than one at higher pressures. For easily condensable gases like CO_2, there is a large dip at lower pressures and then a continuous increase with increase in pressure. Further, the deviations decrease with increase in temperature. At best, real gases behave in a nearly ideal manner only at low pressures and high temperatures.

3.2 CAUSES FOR DEVIATIONS

For ideal gases, it has been assumed that

(i) The volume occupied by molecules is negligible in comparison to the total volume of the gas.

(ii) There are no interactions between molecules.

However, in a real gas, molecules always have definite volume and there are also interactions between them. The magnitude of both these quantities determines the deviation.

3.3 CORRECTIONS FOR DEVIATIONS: VAN DER WAALS EQUATION

Van der Waals introduced two correction terms in the ideal gas equation.

Correction for Volume

Due to the intrinsic volume of molecules, the entire space is not available for the free movement of molecules. He introduced the term b which represents the *effective volume* or *co-volume* occupied by all the molecules in one mole of a gas. Hence, the volume in the ideal gas equation should be replaced by free volume.

For n moles of the gas, the free or corrected volume is

$$V_{corrected} = V - nb$$

The numerical value of b is four times the actual volume occupied by the gas molecules.

Correction for Pressure

Due to intermolecular forces, the observed pressure is less than the pressure which the gas would have exerted if there were no interactions. Van der Waals introduced a correction term an^2/V^2, for n moles of a gas, for intermolecular forces, so that the pressure in the ideal gas equation is replaced by

$$p_{corrected} = p + \frac{an^2}{V^2}$$

where a is a parameter which measures the forces of attraction between the molecules.

The van der Waals equation becomes

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT \tag{3.1}$$

The parameters a and b are called van der Waals parameters, and their values depend upon the nature of the gas. The units of a are atm l^2 mol^{-2} (SI units: Pa m^6 mol^{-2} or N m^4 mol^{-2}) and of b are l mol^{-1} (SI units: m^3 mol^{-1}).

3.4 APPLICABILITY OF VAN DER WAALS EQUATION

The van der Waals equation for one mole of gas is reduced to

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$

At Low Pressures

At low pressures, the volume is sufficiently large. b can be neglected in comparison to V so that

$$\left(p + \frac{a}{V^2}\right)V = RT$$

or $\quad pV = RT - \frac{a}{V}$

or $\quad \frac{pV}{RT} = Z = 1 - \frac{a}{RTV}$

Thus, at low pressures, Z is less than one and, as pressure increases (V decreases), the term a/VRT increases. Consequently, Z decreases with increase of p.

At High Pressures

When p is high, V will be small so that b cannot be neglected. a/V^2 may be considered negligible in comparison to p, so that

$$p(V - b) = RT$$

or $\quad pV = RT + pb$

or $\quad \frac{pV}{RT} = Z = 1 + \frac{pb}{RT}$

Thus, Z is greater than 1 and increases as pressure increases.

At High Temperature and Low Pressure

If temperature is high V is very large, b as well as a/V^2 may be neglected so that the equation reduces to the ideal gas equation.

Exceptional Behaviour of Hydrogen and Helium

In case of H_2 and He, intermolecular forces of attraction are extremely weak and a/V^2 is negligible at all pressures. Hence Z is always greater than one and increases with increase of p as at high pressures.

3.5 EQUATIONS OF STATE FOR REAL GASES

To describe the behaviour of real gases, a number of equations of state have been proposed. A few important ones are given below :

Berthelot equation $$\left(p+\frac{n^2a}{TV^2}\right)(V-nb) = nRT \tag{3.2}$$

Dieterici equation $$(pe^{na/VRT})(V-nb) = nRT \tag{3.3}$$

Clausius equation $$\left(p+\frac{an^2}{T(V+C)^2}\right)(V-nb) = RT \tag{3.4}$$

Virial equation $$pV = nRT\left(1+\frac{Bn}{V}+\frac{Cn^2}{V^2}+\frac{Dn^3}{V^3}+\dots\right) \tag{3.5}$$

or $$pV_m = RT\left(1+\frac{B}{V_m}+\frac{C}{V_m^2}+\dots\right) \tag{3.5a}$$

Equation (3.5) was proposed by Kammerlingh Onnes and is the most general equation. The quantities $B, C, D, \dots$ are called second, third, fourth, etc. virial coefficients and their values depend on the temperature and nature of the gas.

EXAMPLE 3.1 For oxygen gas, the van der Waals parameter b is 0.0318 l mol^{-1}. Estimate the diameter of the oxygen molecule.

Solution Van der Waals parameter

$$b = 4\times \text{volume occupied by molecules in 1 mole of gas}$$
$$= 4\times N_a\times \frac{4}{3}\pi r^3$$

or $$r = \left(\frac{3b}{16\pi N_a}\right)^{\frac{1}{3}}$$

$$b = 0.0318\ l\ \text{mol}^{-1} = 0.0318\times 10^3\ \text{cm}^3\ \text{mol}^{-1}$$

$$r = \left(\frac{3\times 0.0318\times 10^3}{16\times 3.14\times 6.022\times 10^{23}}\right)^{\frac{1}{3}}\ \text{cm}$$
$$= 1.47\times 10^{-8}\ \text{cm}$$

Diameter of oxygen molecule $= 2\times 1.47\times 10^{-8}$
$$= 2.94\times 10^{-8}\ \text{cm}$$

EXAMPLE 3.2 A vessel of 25 *l* capacity contains 10 mol of steam under 50 atm pressure. Calculate the temperature of steam using the van der Waals equation, if, for water,

$$a = 5.46 \text{ atm } l^2 \text{ mol}^{-2} \text{ and } b = 0\ 031\ l \text{ mol}^{-1}$$

Solution The van der Waals equation is

$$\left(p+\frac{n^2a}{V^2}\right)(V-nb) = nRT$$

or

$$T = \left(p+\frac{n^2a}{V^2}\right)(V-nb)/nR$$

$$p = 50 \text{ atm}, n = 10 \text{ mol}, V = 25\ l, a = 5.46, b = 0.031$$

$$T = \left(50 + \frac{100 \times 5.46}{(25)^2}\right)\frac{(25 - 10 \times 0.031)}{10 \times 0.082}$$

$$= 1531.7 \text{ K}$$

EXAMPLE 3.3 (SI units) Calculate the pressure exerted by 0.8 mol of NO_2 which occupies 20 dm³ at 300 K by using (i) the ideal gas equation, (ii) the van der Waals equation with $a = 0.535 \text{ N m}^4 \text{ mol}^{-2}$ and $b = 4.42 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, and (iii) by assuming that it is a mixture of NO_2 and N_2O_4 and 20% of NO_2 is dimerised (assume ideal behaviour).

Solution (i) According to the ideal gas equation

$$pV = nRT$$

or

$$p = \frac{nRT}{V}$$

$$n = 0.8 \text{ mol}, T = 300 \text{ K}, V = 20 \text{ dm}^3 = 20 \times 10^{-3} \text{ m}^3$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$p = \frac{(0.8 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{(20 \times 10^{-3} \text{ m}^3)}$$

$$= 9.98 \times 10^4 \text{ N m}^{-2} \qquad (\text{J} = \text{N m})$$

(ii) According to the van der Waals equation

$$p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$$

$$= \frac{(0.8 \text{ mol}) \times (8.314 \text{ N m mol}^{-1}\text{K}^{-1}) \times 300\text{K}}{(20 \times 10^{-3} - 0.8 \times 4.42 \times 10^{-5})\text{m}^3}$$

$$- \frac{(0.8 \text{ mol})^2 \times (0.535 \text{ N m}^4 \text{ mol}^{-2})}{(20 \times 10^{-3} \text{ m}^3)^2}$$

$$= 9.99 \times 10^4 - 0.09 \times 10^4$$

$$= 9.9 \times 10^4 \text{ N m}^{-2}$$

(iii) If it is a mixture of NO_2 and N_2O_4

$$2NO_2 \rightleftharpoons N_2O_4$$

If 20% NO_2 is dimerised, then

Moles of NO_2, $$n\left(NO_2\right) = 0.8 \times \frac{80}{100} = 0.64$$

Moles of N_2O_4, $$n\left(N_2O_4\right) = \frac{0.16}{2} = 0.08$$

Total number of moles, $n(N_2O_4) + n(NO_2) = 0.08 + 0.64 = 0.72$

$$p = \frac{(0.72 \text{ mol}) \times (8.314 \text{ N m mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K})}{20 \times 10^{-3} \text{ m}^3}$$

$$= 8.98 \times 10^4 \text{ N m}^{-2}$$

3.6 CONDENSATION OF GASES AND CRITICAL CONSTANTS

Gases can be converted into liquids at sufficiently low temperatures and high pressures. Liquefaction of gases occurs when the forces of attraction overcome the thermal agitation of molecules. However, it is an interesting observation that a gas does not liquefy above a certain characteristic temperature however high the pressure may be. This characteristic temperature is called the critical temperature. Thus, *critical temperature* (T_c) is the temperature above which a gas cannot be liquefied, however high the pressure may be.

The minimum pressure which is just sufficient to liquefy the gas at the critical temperature is called the *critical pressure* (p_c).

The volume occupied by one mole of a gas at critical temperature and critical pressure is called the *critical volume* (V_c).

T_c, p_c and V_c are called critical constants. The critical point is a point of inflection in the gas isotherm at critical temperature. Hence,

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0$$

3.7 VAN DER WAALS EQUATION AND THE CRITICAL STATE

If the isotherm is represented by the van der Waals equation, the critical constant can be expressed in terms of van der Waals constants, using Equation (3.1), as

$$p = \frac{RT}{V-b} - \frac{a}{V^2}$$

Differentiating p with respect to V (T constant) and substituting at the inflection point:

$$p = p_c, \quad T = T_c \text{ and } V = V_c$$

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0$$

or $$\frac{RT_c}{(V_c-b)^2} = \frac{2a}{V_c^3}$$

and $$\left(\frac{d^2 p}{dV^2}\right)_{T_c} = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0$$

or $$\frac{2RT_c}{(V_c-b)^3}=\frac{6a}{V_c^4}$$

Solving these equations, we get

$$V_c=3b, \quad p_c=\frac{a}{27\,b^2}, \quad T_c=\frac{8a}{27\,Rb} \tag{3.6}$$

If the values of the critical constants for a gas are known, it is possible to calculate the values of a and b as:

$$a=3P_c\,V_c^2 \quad \text{and} \quad b=\frac{V_c}{3} \tag{3.7}$$

3.8 LAW OF CORRESPONDING STATES

Let us define new variables, called reduced pressure (p_r), reduced volume (V_r) and reduced temperature (T_r) by the equations:

$$p_r=\frac{p}{p_c}, \quad V_r=\frac{V}{V_c}, \quad T_r=\frac{T}{T_c}$$

If these are introduced in the van der Waals equation, it will lead to a single equation :

$$\left(p_r+\frac{3}{V_r^2}\right)\left(3V_r-1\right)=8\,T_r$$

which is valid for all gases and is known as the *equation of corresponding state.* According to this, if two gases have the same values of reduced pressure and reduced temperature, they will have the same reduced volume.

EXAMPLE 3.4 The van der Waals constants for CH_4 are a = 2.25 atm l^2 mol^{-2} and b = 0.043 l mol^{-1}. Calculate its critical constants.

Solution

$$V_c=3b \quad =3\times 0.043=0.129\ l\ \text{mol}^{-1}$$

$$p_c=\frac{a}{27b^2}=\frac{2.25\ \text{atm}\ l^2\ \text{mol}^{-2}}{27\times(0.043\ l\ \text{mol}^{-1})^2}=45.07\ \text{atm}$$

$$T_c=\frac{8a}{27\ Rb}=\frac{8\times(2.25\ \text{atm}\ l^2\ \text{mol}^{-2})}{27\times(0.082\ \text{atm}\ l\ \text{mol}^{-1}\,\text{K}^{-1})\times(0.043\ l\ \text{mol}^{-1})}$$
$$=189.1\ \text{K}$$

EXAMPLE 3.5 Calculate the van der Waals constants a and b for CO_2 (T_c = 304.2 K, p_c = 72.8 atm)

Solution

$$p_c=\frac{a}{27\,b^2}, \quad T_c=\frac{8a}{27\ Rb}$$

or $$\frac{p_c}{T_c}=\frac{a}{27\,b^2}\times\frac{27Rb}{8\,a}=\frac{R}{8\,b} \quad \text{or} \quad b=\frac{RT_c}{8\,p_c}$$

$$T_c = 304.2 \text{ K}, \quad p_c = 72.8 \text{ atm}, \quad R = 0.082\, l \text{ atm mol}^{-1} \text{ K}^{-1}$$

$$b = \frac{(0.082\, l \text{ atm mol}^{-1} \text{ K}^{-1}) \times (304.2 \text{ K})}{8 \times (72.8 \text{ atm})} = 0.0428\, l \text{ mol}^{-1}$$

Now
$$\begin{aligned} a &= 27\, p_c\, b^2 \\ &= 27 \times (72.8 \text{ atm}) \times (0.0428\, l \text{ mol}^{-1})^2 \\ &= 3.60 \text{ atm } l^2 \text{ mol}^{-2} \end{aligned}$$

EXAMPLE 3.6 What will be the reduced pressure, volume and temperature, of methane when one mole of gas is contained in a 5 dm³ flask under 5 atm pressure? What will be the temperature of the gas? The critical constants of methane are:

$$T_c = 190.2 \text{ K}, \qquad V_c = 0.0988\, l \text{ mol}^{-1}, \qquad p_c = 45.6 \text{ atm}$$

Solution

$$p_r = \frac{p}{p_c} = \frac{5}{45.6} = 0.1096$$

$$V_r = \frac{V}{V_c} = \frac{5}{0.0988} = 50.607$$

Now
$$\left(p_r + \frac{3}{V_r^2}\right)\left(3V_r - 1\right) = 8\, T_r$$

or
$$\begin{aligned} T_r &= \frac{\left(p_r + \frac{3}{V_r^2}\right)\left(3\, V_r - 1\right)}{8} \\ &= \frac{\left[0.1096 + \frac{3}{(50.607)^2}\right]\left[3 \times 50.607 - 1\right]}{8} \\ &= 2.089 \end{aligned}$$

Since
$$T_r = \frac{T}{T_c}$$
$$\begin{aligned} T = T_r \times T_c &= 2.089 \times 190.2 \\ &= 397.3 \text{ K} \end{aligned}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 3.7 The critical volume and pressure of He are

$$V_c = 57.8 \text{ cm}^3 \text{ mol}^{-1}, \qquad p_c = 2.26 \text{ atm}$$

Calculate the van der Waals parameters a and b and estimate the radius of the helium atom.

Solution

$$b = \frac{V_c}{3}, \qquad a = 3\, p_c\, V_c^2$$

$$b = \frac{57.8}{3} = 19.27 \text{ cm}^3 \text{ mol}^{-1} = 0.0193 \text{ dm}^3 \text{ mol}^{-1}$$

$$a = 3 \times (2.26 \text{ atm}) \times (57.8 \text{ cm}^3 \text{ mol}^{-1})^2$$
$$= 2.27 \times 10^4 \text{ cm}^6 \text{ atm mol}^{-2} = 0.0227 \text{ dm}^6 \text{ atm mol}^{-2}$$

Now, $b \approx 4 \times$ Volume occupied by Avogadro's number of molecules

or $b = 4 \times V_m$

Volume of one molecule, $V = \dfrac{b}{4N_a}$

$$= \frac{0.0193}{4 \times 6.02 \times 10^{23}} = 8.01 \times 10^{-27} \text{ dm}^3$$
$$= 8.01 \times 10^{-30} \text{ m}^3$$

$$V = \frac{4}{3} \pi r^3$$

or
$$r = \left(\frac{3V}{4\pi}\right)^{\frac{1}{3}}$$
$$= \left(\frac{3 \times 8.01 \times 10^{-30} \text{ m}^3}{4 \times 3.14}\right)^{\frac{1}{3}} = 1.24 \times 10^{-10} \text{ m} = 1.24 \text{ Å}$$

EXAMPLE 3.8 The critical temperature (T_c) and pressure (p_c) for O_2 and Cl_2 are

	T_c	p_c
O_2	155 K	5.0×10^6 N m^{-2}
Cl_2	417 K	7.6×10^6 N m^{-2}

Which gas has

(a) the smaller value of van der Waals parameter a
(b) the smaller value of van der Waals parameter b
(c) the smaller critical volume ?

Solution

(a) Since $p_c = \dfrac{a}{27 b^2}$, $T_c = \dfrac{8a}{27 Rb}$

$$\frac{p_c}{T_c} = \frac{a}{27 b^2} \times \frac{27 Rb}{8a} = \frac{R}{8b}$$

or
$$b = \frac{RT_c}{8 p_c}$$

$\therefore$
$$b(O_2) = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (155 \text{ K})}{8 \times (5.0 \times 10^6 \text{ N m}^{-2})} = 3.22 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

and
$$b(Cl_2) = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (417 \text{ K})}{8 \times (7.6 \times 10^6 \text{ N m}^{-2})} = 5.70 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Hence b for O_2 is less than b for Cl_2

(b) Since $a = 27\, p_c\, b^2$

$\therefore$
$$a(O_2) = 27 \times (5.0 \times 10^6 \text{ N m}^{-2}) \times (3.22 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})^2$$
$$= 0.140 \text{ N m}^4 \text{ mol}^{-2}$$
$$a(Cl_2) = 27 \times (7.6 \times 10^6 \text{ N m}^{-2}) \times (5.70 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1})^2$$
$$= 0.667 \text{ N m}^4 \text{ mol}^{-2}$$

Hence, a for O_2 is less than a for Cl_2

(c) Since $V_c = 3b$

$$V_c\,(O_2) = 3 \times (3.22 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}) = 9.66 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

and $$V_c\,(Cl_2) = 3 \times (5.70 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}) = 17.1 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

Hence V_c for O_2 is less than V_c for Cl_2.

EXAMPLE 3.9 The van der Waals parameters a and b for some gases are

Gas	a (dm^6 atm mol^{-2})	b (dm^3 mol^{-1})
Hydrogen	0.244	0.026
Helium	0.034	0.024
Nitrogen	1.390	0.039

(a) Estimate the critical temperatures and pressures for these gases.

(b) Estimate the temperature and pressure that 1 mole of He and N_2 will have in states corresponding to 1 mole of hydrogen at 25°C and 1 atm.

Solution (a) The critical temperature and pressure can be calculated as:

(i) For hydrogen:

$$p_c = \frac{a}{27\,b^2} = \frac{(0.244\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.026\ \text{dm}^3\ \text{mol}^{-1})^2} = 13.37\ \text{atm}$$

$$T_c = \frac{8\,a}{27\,Rb} = \frac{8 \times (0.244\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.082\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (0.026\ \text{dm}^3\ \text{mol}^{-1})}$$
$$= 33.9\ \text{K}$$

(ii) For helium:

$$p_c = \frac{a}{27\,b^2} = \frac{(0.034\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.024\ \text{dm}^3\ \text{mol}^{-1})^2} = 2.18\ \text{atm}$$

$$T_c = \frac{8\,a}{27\,Rb} = \frac{8 \times (0.034\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.082\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (0.024\ \text{dm}^3\ \text{mol}^{-1})}$$
$$= 5.12\ \text{K}$$

(iii) For nitrogen:

$$p_c = \frac{a}{27\,b^2} = \frac{(1.390\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.039\ \text{dm}^3\ \text{mol}^{-1})^2} = 33.85\ \text{atm}$$

$$T_c = \frac{8\,a}{27\,Rb} = \frac{8 \times (1.390\ \text{dm}^6\ \text{atm mol}^{-2})}{27 \times (0.082\ \text{dm}^3\ \text{atm mol}^{-1}\ \text{K}^{-1}) \times (0.039\ \text{dm}^3\ \text{mol}^{-1})}$$
$$= 128.8\ \text{K}$$

(b) The gases are in corresponding states when their reduced temperatures have the same values. The reduced temperature and pressure of H_2 at 1 atm and 298 K can be calculated as

$$p_r = \frac{1}{13.37} = 0.075, \qquad T_r = \frac{298}{33.9} = 8.79$$

Thus, the temperature and pressure for He and N_2 to have same T_r and P_r in corresponding states are

(i) Helium $T = T_r \times T_c = 8.79 \times 5.12 = 45$ K

$p = p_r \times p_c = 0.075 \times 2.18 = 0.16$ atm

(ii) Nitrogen $T = T_r \times T_c = 8.79 \times 128.8 = 1132.2$ K

$p = p_r \times p_c = 0.075 \times 33.85 = 2.54$ atm

EXAMPLE 3.10 (a) Express the van der Waals equation as a virial expression in powers of $1/V$. Calculate the second and third virial coefficients in terms of van der Waals parameters.

(b) Calculate the values of the second and third virial coefficients for nitrogen at 27°C when $a = 1.390$ dm^6 atm mol^{-2} and $b = 3.913 \times 10^{-2}$ dm^3 mol^{-1}.

Solution The van der Waals equation for one mole of gas is

$$\left(p + \frac{a}{V^2}\right)\left(V - b\right) = RT$$

or

$$p = \frac{RT}{V - b} - \frac{a}{V^2}$$

or

$$p = \frac{RT}{V}\left[\frac{1}{1 - \left(\frac{b}{V}\right)}\right] - \frac{a}{V^2}$$

The term $\dfrac{1}{1 - \left(\frac{b}{V}\right)}$ can be expanded as

$$\frac{1}{1 - x} = 1 + x + x^2 + \dots \quad \text{where } x = \frac{b}{V}$$

$$p = \frac{RT}{V}\left[1 + \frac{b}{V} + \left(\frac{b}{V}\right)^2 + \dots\right] - \frac{a}{V^2}$$

$$= \frac{RT}{V}\left[1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \left(\frac{b}{V}\right)^2 \dots\right]$$

Comparing with the virial equation

$$p = \frac{RT}{V}\left[1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}\right]$$

we get

$$B = b - \frac{a}{RT} \quad \text{and} \quad C = b^2$$

where B and C are second and third virial coefficients.

(b) For nitrogen, $a = 1.390$ dm^6 atm mol^{-2}, $b = 0.03913$ dm^3 mol^{-1}

Now the second virial coefficient

$$B = b - \frac{a}{RT}$$

or
$$B = 0.03913 - \frac{1.390}{0.082 \times 300}$$
$$= -\ 0.0174\ \text{dm}^3\ \text{mol}^{-1} = -\ 17.4\ \text{cm}^3\ \text{mol}^{-1}$$

Third virial coefficient
$$C = b^2$$
$$= (0.03913\ \text{dm}^3\ \text{mol}^{-1})^2$$
$$= 1.531 \times 10^{-3}\ \text{dm}^6\ \text{mol}^{-2} = 1531\ \text{cm}^6\ \text{mol}^{-2}$$

EXAMPLE 3.11 Show that the excluded volume is four times the actual volume of a molecule.

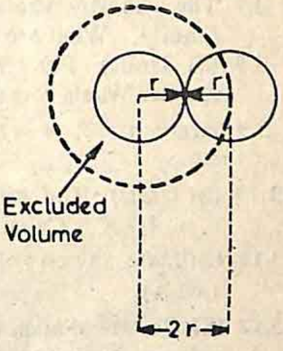

FIG. 3.2 *Excluded volume per pair of molecules.*

Solution If we assume the molecules to be spheres of radius r, then the volume of a molecule is $4/3\ \pi\ r^3$. The closest approach of two molecules is $2\,r$. Therefore, the two molecules cannot approach each other more closely than the distance $2r$. Thus, if we consider only bimolecular collisions, then the volume occupied by a sphere of radius $2r$ represents the excluded volume per pair of molecules, as shown in Fig. 3.2 Thus,

$$\text{Excluded volume per pair of molecules} = \frac{4}{3}\pi\left(2r\right)^3$$

$$\text{Excluded volume per molecule} = \frac{1}{2}\left[\frac{4}{3}\pi\left(2\,r\right)^3\right]$$
$$= \frac{1}{2}\left[8 \times \frac{4}{3}\pi r^3\right]$$
$$= 4 \times \frac{4}{3}\pi\, r^3$$
$$= 4 \times \textbf{Volume occupied by a molecule}$$

QUESTIONS

Numerical Problems

3.1 The compressibility factor $\left(Z = \frac{PV}{nRT}\right)$ for a gas at 0°C and 100 atm is 0.2013. Calculate the volume occupied by 0.2 mol of the gas at 100 atm and 0°C.

3.2 (SI Units) Calculate the pressure exerted by 0.150 mol of SO_2 at 300 K, which occupies $4.50 \times 10^{-4}\ \text{m}^3$, using the van der Waals equation ($a = 0.680\ \text{N m}^4\ \text{mol}^{-2}$, $b = 5.64 \times 10^{-5}\text{m}^3\ \text{mol}^{-1}$). Calculate the pressure which SO_2 would exert if it behaved ideally.

3.3 Compare the temperature of 3 mol of SO_2 at 15 atm occupying a volume of 10 dm^3, obtained by the ideal gas equation and van der Waals' equation ($a = 6.7$ atm $\text{dm}^6\ \text{mol}^{-2}$ and $b = 0.0564\ \text{dm}^3\ \text{mol}^{-1}$).

3.4 A boy was asked to calculate the pressure of one mole of a non-ideal gas (CO_2) at 310 K occupying 6 l ($a = 3.60$ atm l^2 mol^{-2} and $b = 0.043$ l mol^{-1}). He calculated the pressure by using the ideal gas equation. What is the percentage error?

3.5 The van der Waals parameters for a gas are $a = 3.0$ atm l^2 mol^{-2} and $b = 0.05$ l mol^{-1}. Calculate the pressure of the gas from (i) the ideal gas equation and (ii) the van der Waals equation, if one mole of the gas at 127°C has a volume of 1.5 l.

3.6 The critical constants of CCl_4 are:

$$T_c = 556.2 \text{ K}, \quad p_c = 45.0 \text{ atm and } V_c = 275.8 \text{ ml}$$

Calculate the van der Waals constants a and b.

3.7 The van der Waals constants for N_2 are $a = 1.39$ atm l^2 mol^{-2} and $b = 0.039$ l mol^{-1}. What are the critical constants of N_2?

3.8 (SI Units) For SO_2 $T_c = 430$ K and $p_c = 7.6 \times 10^6$ N m^{-2}. Calculate the van der Waals constants a and b.

3.9 Argon has $T_c = -122$°C and $P_c = 48$ atm. Estimate the radius of the argon atom.

3.10 (SI Units) The critical constants for chlorine are $p_c = 7.6 \times 10^6$ N m^{-2} and $T_c = 417$ K. Calculate the van der Waals constants a and b.

3.11 Estimate the co-volume for one mole of neon (assume the radius of neon to be 1.60 Å).

3.12 (SI Units) Which of the two, CO_2 or CH_4, has the larger molar excluded volume, given that $d\,(CO_2) = 4.49 \times 10^{-10}$ m and $d\,(CH_4) \leqslant 3.82 \times 10^{-10}$ m.

3.13 At 100°C and 200 atm, the compressibility factor of N_2 is 1.10. Calculate the weight of N_2 necessary to fill a gas cylinder of 50 l capacity under the given conditions.

3.14 The reduced temperature and volume of a gas are 0.7 and 0.02 respectively. What will be its pressure if its critical pressure is 42 atm.

3.15 Calculate T_r, V_r and p_r of CO_2 when one mole of gas is present in a 2 dm^3 flask under 5 atm pressure. The critical constants of CO_2 are: $T_c = 304.2$ K, $p_c = 72.8$ atm, $V_c = 0.094$ l mol^{-1}.

3.16 Calculate the volume occupied by 2.5 mol of N_2 at 273 K and 100 atm pressure if $\dfrac{p_cV_c}{RT_c} = 3/8$ and $\dfrac{p_rV_r}{T_r} = 2.2$.

3.17 The critical volume and pressure of noble gases are:

Gas	V_c (dm^3 mol^{-1})	p_c (atm)
He	0.058	2.26
Ne	0.042	26.9
Ar	0.073	48.0
Xe	0.119	58.0

(i) Which of these has the smaller value of b?

(ii) Arrange the van der Waals constant a in decreasing order.

3.18 The critical temperature and pressure data for some gases are:

Gas	T_c (K)	p_c (N m^{-2})
CO_2	304	7.3×10^6
Cl_2	417	7.6×10^6
H_2	38	2.0×10^6

Which of these has the largest and which has the smallest critical volume?

3.19 Calculate the second (B) and third (C) virial coefficients for methane and ethane at 27°C. The values of a and b are:

CH_4 : $a = 2.253$ dm^6 atm mol^{-2}, $b = 0.043$ dm^3 mol^{-1}

C_2H_6 : $a = 4.471$ dm^6 atm mol^{-2}, $b = 0.057$ dm^3 mol^{-1}

3.20 The van der Waals constants a and b are:

	a (dm^6 atm mol^{-2})	b (dm^3 mol^{-1})
Oxygen	1.360	0.0318
Ammonia	4.170	0.0371
Methane	2.253	0.0428

Estimate the pressure and temperature that 1 mol of ammonia and methane will have in states corresponding to 1 mol of oxygen at 27°C and 1 atm.

QUIZ QUESTIONS

Type A: Multiple Choice

3.21 Which one of the following equations correctly represents the van der Waals equation?

(a) $\left(p - \frac{an^2}{V^2}\right)(V-b) = nRT$

(b) $\left(p + \frac{an^2}{V}\right)(V-nb) = nRT$

(c) $\left(p - \frac{an^2}{V}\right)(V-nb) = nRT$

(d) $\left(p + \frac{an^2}{V^2}\right)(V-nb) = nRT$

3.22 The SI units of the van der Waals parameter a are

(a) Pa m^3 mol^{-2} (b) N m^6 mol^{-2}

(c) J m^6 mol^{-2} (d) Pa m^6 mol^{-2}

3.23 A real gas obeying the van der Waals equation will closely resemble an ideal gas if

(a) the parameters a and b are small

(b) a is large but b is small

(c) a is small but b is large

(d) both a and b are large

3.24 The SI units of the van der Waals b term are

(a) m^3 mol (b) m^2 mol^{-1}

(c) m^3 mol^{-1} (d) m^2 mol

3.25 At extremely low pressures, the van der Waals equation for one mole may be written as

(a) $pV = RT + Pb$

(b) $pV = RT - \frac{a}{V}$

(c) $(p + a)(V-b) = RT$

(d) $pV = RT$

3.26 The critical pressure (p_c) and reduced pressure (p_r) are related as

(a) $p \times p_r = p_c$

(b) $p_r \times p_c = p$

(c) $p \times p_c = p_r$

(d) $p_r \times p_c \times p = 1$

3.27 If, p_r, V_r and T_r are the reduced pressure, volume and temperature, respectively, then the van der Waals equation for corresponding states is

(a) $\left(p_r + \frac{3}{V_r^2}\right)(V_r - 1) = \frac{8}{3} T_r$

(b) $\left(p_r + \frac{1}{V_r^2}\right)(3 V_r - 1) = 8 T_r$

(c) $\left(p_r + \frac{3}{V_r^2}\right)(3 V_r - 1) = 8 T_r$

(d) $\left(p_r + \frac{3}{V_r^2}\right)(8 V_r - 1) = 3 T_r$

3.28 The value of the compressibility factor $(Z) = \frac{pV}{nRT}$ for an ideal gas is equal to
(a) R (b) 1.5 (c) 2 (d) 1

3.29 A gas obeys the van der Waals equation. It will approach ideality at
(a) high pressures
(b) low values of pV products
(c) extremely low pressures
(d) low temperatures

3.30 A gas obeys the van der Waals equation with $T_c = 450$ K, $p_c = 50$ atm. The compressibility factor pV/nRT will be greater than unity at
(a) 20 atm and 350 K
(b) 25 atm and 600 K
(c) 100 atm and 600 K
(d) 100 atm and 300 K

Type B: Multiple Choice (Numerical Problems)

3.31 The van der Waals constants b for four gases are:

Gas	*A*	*B*	*C*	*D*
b (l mol^{-1})	0.039	0.028	0.123	0.043

Which gas will have the largest excluded volume?
(a) *A* (b) *B* (c) *C* (d) *D*

3.32 The van der Waals constants for some gases are:

Gas	a (l^2 atm mol^{-2})	b (l mol^{-1})
NH_3	4.17	0.037
CO_2	3.59	0.043
CH_4	2.25	0.043
O_2	1.36	0.032

The gas with the highest critical temperature is
(a) NH_3 (b) CO_2 (c) CH_4 (d) O_2

3.33 The critical temperature and pressure of a gas are 400 K and 41 atm, respectively. The critical volume is
(a) 4.6 l mol^{-1}
(b) 0.9 l mol^{-1}
(c) 0.3 l mol^{-1}
(d) 400/41 l mol^{-1}

3.34 The critical constants for a gas are

$p_c = 125$ atm
$V_c = 90$ dm^3 mol^{-1}
$T_c = 574$ K

The van der Waals parameter b is equal to

(a) $\dfrac{(125)^2 \times 574}{90}$ dm^3 mol^{-1}

(b) $\dfrac{125 \times 27}{574}$ dm^3 mol^{-1}

(c) 30 dm^3 mol^{-1}

(d) 3×10^6 dm^3 mol^{-1}

3.35 The van dar Waals parameters for C_2H_6 are $a = 0.56$ N m^4 mol^{-2} and $b = 6.4 \times 10^{-5}$ m^3 mol^{-1}. The critical volume (V_c, dm^3 mol^{-1}) of C_2H_6 is

(a) 0.192

(b) $6.4 \times 0.56 \times 10^{-5}$

(c) $\dfrac{6.4}{0.56} \times 10^{-5}$

(d) $\dfrac{6.4 \times 10^{-5}}{0.082 \times 0.56}$

3.36 The critical volume and critical pressure of a gas are 0.06 l mol^{-1} and 200 atm, respectively. The value of the van der Waals parameter a (l^2 atm mol^{-2}) is

(a) 120 (b) 1.20 (c) 0.24 (d) 0.0024

3.37 The van der Waals parameter b for H_2O is 0.030 dm^3 mol^{-1}. The reduced volume of one mole of gas contained in a 0.9 dm^3 flask under 5 atm pressure is

(a) 9 (b) 10 (c) 0.09 (d) 0.081

3.38 p_cV_c/RT_c is equal to

(a) 0.375 (b) 8.314 (c) 1.987 (d) 0.082

3.39 The critical temperature and reduced temperature of a gas are 150 K and 3, respectively. The temperature of the gas is

(a) 50 K (b) 150 K (c) 300 K (d) 460 K

3.40 For a gas, $T_c = 192$ K, $b = 0.03$ l mol^{-1}. What will be the critical pressure (assume $R = 0.08$ l atm mol^{-1})

(a) 72 atm (b) 512 atm

(c) 64 atm (d) 0.125 atm

Type C: True or False

3.41 Gases can be liquefied above their critical temperature only by applying very high pressures.

3.42 Rise in compressibility factor with increasing pressure is due the van der Waals parameter a.

3.43 Easily condensable gases have comparatively higher values of the van der Waals parameter a.

3.44 A gas can be liquefied at critical temperature if reduced pressure is less than one.

3.45 The term n^2a/V^2 in the van der Waals equation is a measure of the intermolecular forces.

3.46 The critical temperature is proportional to b/a.

3.47 The gas with a larger value of T_c/p_c will have larger excluded volume.

3.48 The compressibility factor for hydrogen and helium is less than one at all pressures.

3.49 A gas with $T_c = 350$ K and $p_c = 50$ atm cannot be liquefied at 300 K and 50 atm.

3.50 The critical volume can be calculated by dividing the molar mass by the critical density.

ANSWERS

Numerical Problems

3.1 $Z = \dfrac{pV}{nRT}$ so that $V = \dfrac{ZnRT}{p} = \dfrac{0.2013 \times 0.2 \times 0.082 \times 273}{100} = 9.01 \times 10^3\ l$

3.2 7.73×10^5, 8.24×10^5 N m^{-2} *3.3* 609.7 K, 623.5 K *3.4* 2.39% *3.5* (i) 21.867 atm (ii) 21.29 atm *3.6* 10.33 atm l^2 mol^{-2}, 0.0919 l mol^{-1} *3.7* $V_c = 0.117\ l$. $p_c = 33.85$ atm, $T_c = 128.8$ K *3.8* $a = 0.709$, $b = 5.88 \times 10^{-5}$ m^3 mol^{-1} *3.9* 1.469×10^{-8} cm *3.10* $a = 0.667$ N m^4 mol^{-2}, $b = 5.7 \times 10^{-5}$ m^3 mol^{-1} *3.11* 0.0412 dm^3 mol^{-1} *3.12* For $CO_2 = 1.89 \times 10^{-28}$m^3, for $CH_4 = 1.17 \times 10^{-28}$ m^3 *3.13* 4.16 kg *3.14* 6.72 atm *3.15* $p_r = 0.069$, $V_r = 21.28$, $T_r = 4.75$ *3.16* 0.462 *3.17* (i) Ne (ii) Xe > Ar > Ne > He *3.18* Cl_2, H_2 *3.19* CH_4: $B = -0.57$, $C = 1.85 \times 10^{-3}$; C_2H_6: $B = -0.125$, $C = 3.25 \times 10^{-3}$ *3.20* NH_3: 2.24, 787.9 ; CH_4 : 0.91, 369.0

QUIZ QUESTIONS

3.21 (d) *3.22* (d) *3.23* (a) *3.24* (c) *3.25* (d) *3.26* (b) *3.27* (c) *3.28* (d) *3.29* (c) *3.30* (c) *3.31* (c) *3.32* (a): T_c is proportional to a/b and hence NH_3 has largest critical temperature *3.33* (c): $\dfrac{p_cV_c}{RT_c} =, 3/8 \therefore V_c = 3/8 \times \dfrac{400 \times 0.082}{41} = 0.3\ l$ mol^{-1} *3.34* (c) *3.35* (a) *3 36* (c) *3.37* (b) *3.38* (a) *3.39* (d) *3.40* (c) *3.41* False: Gases cannot be liquefied above critical temperature, however high the pressure may be *3.42* False: Rise in compressibility factor with increasing pressure is due to b *3.43* True *3.44* False: A gas can be liquefied at $T = T_c$ if $p \geqslant p_c$ so that $p/p_c = p_c \geqslant 1$ *3.45* True *3.46* False: T_c is proportional to a/b because $T_c = 8\,a/27\,R_b$ *3.47* True: $\dfrac{p_cV_c}{RT_c} = 3/8 \therefore V_c \propto \dfrac{T_c}{p_c}$ and $V_c = 3\,b$: large T_c/p_c means larger b or excluded volume *3.48* False *3.49* True *3.50* True

4

First Law of Thermodynamics

Thermodynamics is the branch of science which deals with energy changes in physical and chemical processes. In general, it is concerned with the interconversion of various forms of energy (heat, mechanical, electrical, chemical energy, etc.) into one another. The basic structure of the subject rests upon its three laws. All other equations in thermodynamics can be deduced logically from these laws.

4.1 SYSTEM AND SURROUNDINGS

The specified portion of the universe under observation is called the *system*. A system is called *homogeneous* if physical properties and chemical composition are identical throughout the system. On the other hand, a *heterogeneous system* consists of parts, each of which has different physical and possibly different chemical properties also. A homogeneous system consists of one phase whereas a heterogeneous system has two or more phases. The rest of the universe which is not a part of the system is called the *surroundings*.

4.2 TYPES OF SYSTEMS

Three commonly encountered systems are defined as:

(a) *Isolated system* A system which can exchange neither energy nor matter with its surroundings.

(b) *Closed system* A system which can exchange energy but not matter with its surroundings.

(c) *Open system* A system which can exchange matter as well as energy with the surrounding.

4.3 STATE OF A SYSTEM

The state of a system is defined by the values of the measurable physical properties of the system. The measurable properties of a macroscopic system which depend only on the state of the system are called *state functions* or *state variables*. For example, pressure, volume, temperature, composition, energy, etc. are state functions. However, it is not necessary to define the values of all the state variables to define the state of the system. For any given system, a certain minimum number of variables are sufficient to define its state.

4.4 EXTENSIVE AND INTENSIVE PROPERTIES

An *extensive property* of a homogeneous system depends upon the amount of substance in the system, for example, mass, volume, energy, etc. For a heterogeneous system consisting of several phases, the total value of the extensive property is equal to the sum of the contributions from the several phases.

An *intensive property* is one which is independent of the amount of substance present in each phase of the system, for example, temperature, pressure, viscosity, chemical potential, etc. At equilibrium, some of the intensive variables have the same value in different phases of the system.

4.5 TYPES OF PROCESSES

A process gives the path or operation by which a system changes from one state to another. In other words, a *process* means a change in at least one of the state variables (property).
Some common types of processes are:

(a) *Isothermal process* A process in which the temperature of the system remains constant.

(b) *Adiabatic process* A process in which no heat can leave or enter the system.

(c) *Isobaric process* A process in which the pressure of the system remains constant.

(d) *Isochoric process* A process in which the volume of the system remains constant.

(e) *Cyclic process* A process which consists of several steps, but the system returns to its original state after undergoing various changes.

(f) *Reversible process* A process in which the direction may be reversed at any stage by merely a small change in a variable like temperature, pressure, etc. The driving force is only infinitesimally greater than the opposing force and is carried out infinitesimally slowly. Therefore, an ideal reversible process may take infinite time.

(g) *Irreversible process* A process which is not reversible is called an irreversible process. The magnitude of the driving force is very different from the opposing force. All natural processes are irreversible.

4.6 WORK, HEAT AND ENERGY

Work, heat and energy have the same units. Whereas energy is a thermodynamic property of the system, work and heat are not properties of the system. Work and heat are meaningful only when a system undergoes a process. The units of energy are erg, calorie or joule. The SI unit of energy is the joule (J) which is equal to newton metre (1 J = 1 N m). The various common units of energy are related as follows:

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg} = 4.184 \text{ J}$$

Work

Work is equal to the force multiplied by the distance through which it acts. Work on or by a system can be performed in a number of ways, e.g. gravitational work, mechanical work, electrical work, etc.

Mechanical work is performed when a system changes its volume against an opposing pressure. If a gas expands against a constant external pressure, p_{ex} and its volume changes by an infinitesimally small amount, dV, then the small amount of work done, dw, on the system is

$$dw = -p_{ex}\, dV$$

If the volume of the system changes by a finite quantity from volume V_1 to V_2, then total work done,

$$W = -\int_{V_1}^{V_2} p_{ex}\, dV$$

If p is constant, $w = -p_{ex}(V_2 - V_1) = -p_{ex} \times \Delta V$

If V is constant, $w = -p_{ex} \times 0 = 0$

It may be noted that the maximum work is done if the process is reversible, i.e, $w_{rev} \geqslant w_{irr}$.

Heat

It is another form of energy which the system can exchange with the surroundings. It flows from higher to lower temperatures.

As a convention, heat absorbed by the system is expressed as q and work done on the system as w. When a system undergoes a change of state, the values of q and w for the process depend on the path, although the change in energy is independent of the path.

Numerical Values of Work and Heat and their Physical Meaning

According to convention, q and w are the heat absorbed and work done on the system. Therefore, when

q is +ve	heat has been added to the system.
q is −ve	heat has flown out of the system.
w is +ve	work has been done on the system.
w is −ve	work has been done by the system.

Note It may be noted that many books use the opposite sign convention for work. Work done by the system is taken as +ve. *However, the latest convention is to take work done on the system as positive.* This concept is related to the internal energy in such a way that work done is +ve if it increases the internal energy of the system. But the old convention is still in use, particularly in engineering textbooks.

Energy of the System

The total energy E_{total} of a system is equal to the internal energy, U, the energy due to the position and energy due to the motion of the system as a whole. For example, a spherical vessel with insulated walls containing some gas, has a certain internal energy. It can also have energy mgh due to its position relative to earth and, if the whole body is moving with a velocity v, also kinetic energy $\frac{1}{2} m v^2$. We shall be interested mostly in changes in internal energy which may be due to heat absorption or work done on it.

EXAMPLE 4.1 (SI units) Calculate the work required to raise a mass of 500 g through a height of 1 m ($g = 9.8$ m s^{-2}).

Solution Work done to raise a mass m through a height h is

$$w = mgh$$

$$m = 500\ \text{g} = 0.5\ \text{kg},\ g = 9.8\ \text{m s}^{-2}\ \text{and}\ h = 1\ \text{m}$$

$$w = (0.5\ \text{kg}) \times (9.8\ \text{m s}^{-2}) \times (1\ \text{m})$$

$$= 4.9\ \text{kg m}^2\text{s}^{-2} = 4.9\ \text{J}$$

EXAMPLE 4.2 One mole of a gas occupying 3 dm^3 is expanded against a constant external pressure of 1 atm to a volume of 15 dm^3. Calculate the work done on the system.

Solution Work done on the system during expansion against constant external pressure is

$$w = -p_{ex}\Delta V = -p_{ex}(V_2 - V_1)$$

$$p_{ex} = 1\ \text{atm},\ V_1 = 3\ \text{dm}^3,\ V_2 = 15\ \text{dm}^3$$

$$w = -(1\ \text{atm}) \times (15 - 3)\ \text{dm}^3$$

$$= -12\ \text{atm dm}^3$$

$$= -12 \times 101.32\ \text{J} = -1.216\ \text{KJ}$$

$$(1\ \text{atm dm}^3 = 101.32\ \text{J})$$

The negative value indicates that the work is done by the system.

Example 4.3 Two moles of an ideal gas at 2 atm and 27°C is compressed isothermally to one half its volume by an external pressure of 4 atm. Calculate w.

Solution Work done on the system,

$$w = -p_{ex}\,(V_2 - V_1)$$

$$p_{ex} = 4 \text{ atm}, \quad V_1 = \frac{nRT}{p}$$

$$= \frac{(1 \text{ mol}) \times (0.082 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K})}{2 \text{ atm}}$$

$$= 24.6 \text{ dm}^3$$

and $V_2 = \dfrac{V_1}{2} = 12.3 \text{ dm}^3$

$$w = -4 \text{ atm} \times (12.3 - 24.6) \text{ dm}^3$$

$$= 49.2 \text{ atm dm}^3$$

$$= 49.2 \times 101.32 \text{ J} = 4.985 \text{ KJ}$$

$$[1 \text{ atm dm}^3 = 101.32 \text{ J}]$$

4.7 FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics states that energy can neither be created nor destroyed although it can be transformed from one form into another.

The law can also be stated in the following alternative ways:

(i) The energy of an isolated system remains constant.

(ii) It is not possible to construct a perpetual-motion machine which can work endlessly without the expenditure of energy.

The first law of thermodynamics has no theoretical proof. It is a law based on human experience and has not yet been violated. Mathematically, for an infinitesimal change, it may be expressed as:

$$dU = đq + đw$$

where $đq$ is the heat gained by the system and $đw$ is the work done on it. It may be noted here that $đq$ and $đw$ represent small changes in heat and work, respectively. '$đ$' should not be confused with differential. It is regarded as *incomplete* or *inexact differential* because q and w are path-dependent. To calculate the total q and w, path must also be specified before integrating. On the other hand, dU is the *complete* or *exact differential*.

For a finite change,

$$\Delta U = q + w$$

Energy is a state function and ΔU depends on initial and final states, whereas q and w depend on the path. However, whatever may be the process, ΔU is always equal to $q + w$ if the initial and final states are well defined.

Note If the old convention of work (i.e. work done by the system is +ve) is considered, the first law may be expressed as $\Delta U = q - w$.

4.8 ENTHALPY OF A SYSTEM

Enthalpy is defined as

$$H = U + pV$$

Since U, p and V are state variables, enthalpy is also a state function, i.e. the change in enthalpy on change of state is independent of the path.

The change in enthalpy may be expressed as

$$\Delta H = \Delta U + \Delta(pV)$$

If the process is carried out at constant pressure

$$\Delta H = \Delta U + p\Delta V$$

or

$$\begin{aligned} dH &= dU + pdV \\ &= q - p\Delta V + pdV \qquad \text{(Here } dU = q - pdV\text{)} \\ &= q_p \end{aligned}$$

i.e., the enthalpy change for a system is equal to the heat absorbed by the system at constant pressure.

4.9 HEAT CAPACITIES

The heat required to raise the temperature of a system by one degree is called its *heat capacity*. For one mole of a pure substance, it is called the molar heat capacity (C_m). Heat capacity is of two types :

Heat capacity at constant volume,

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Heat capacity at constant pressure,

$$C_p = \left(\frac{\partial q}{\partial T}\right)_p = \left(\frac{\partial H}{\partial T}\right)_p$$

For an ideal gas, the difference between C_p and C_V is

$$C_p - C_V = nR$$

or

$$C_{p,m} - C_{V,m} = R \qquad (n = 1)$$

Thus, for an ideal gas, the molar heat capacity at constant pressure is greater than the molar heat capacity at constant volume by R (8.314 J K^{-1} mol^{-1}).

However, in general, for all states of matter,

$$C_p - C_V = \alpha \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] V$$

or

$$= \frac{\alpha^2}{\beta} TV$$

where α is the thermal expansivity and β is the isothermal compressibility, defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

and

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

EXAMPLE 4.4 Two hundred and eighty grams of nitrogen absorbs 100 cal of heat without change in volume. In doing so, its temperature rises from 30° to 32°C. Calculate ΔU and the molar heat capacity at constant volume.

Solution The gas absorbs heat without change in volume, so that

$$w = 0 \qquad (\because \ \Delta V = 0)$$

Heat absorbed, $q = 100$ cal

Now, $\Delta U = q + w = 100+0 = 100$ cal

Heat capacity at constant volume

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \frac{100 \text{ cal}}{(32-30)^\circ\text{C}}$$

$$= 50 \text{ cal K}^{-1}$$

$$\text{No. of moles of nitrogen} = \frac{280 \text{ g}}{28 \text{ g mol}^{-1}} = 10 \text{ mol}$$

$$\text{Molar heat capacity} = \frac{50 \text{ cal K}^{-1}}{10 \text{ mol}} = 5 \text{ cal K}^{-1} \text{ mol}^{-1}$$

EXAMPLE 4.5 Work done during the expansion of a gas from 4 dm^3 to 6 dm^3, against a constant external pressure of 2 atm, has been used to heat 1 mol of water. What is the final temperature of water if initially it was 293K ? The specific heat of water at 293 K is 4.184 J g^{-1} K^{-1}

Solution Work done on the system, $w = -p_{ex}(V_2 - V_1)$

$$p_{ex} = 2 \text{ atm}, \qquad V_2 = 6 \text{ dm}^3, \qquad V_1 = 4 \text{ dm}^3$$

$$w = -2 \text{ atm} \times (6-4) \text{ dm}^3$$

$$= -4 \text{ atm dm}^3$$

$$= -4 \times 101.32 \text{ J} \quad \text{or} \quad = -405.28 \text{ J}$$

$$[1 \text{ atm dm}^3 = 101.32 \text{ J}]$$

This means, work done by the system = 405.28 J

This work is used up for heating water.

Specific heat of water = 4.184 J K^{-1} g^{-1}

Molar heat capacity of water $= 4.184 \times 18$

$$= 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$$

Now $C_{p,m}\,\Delta T = 405.28$ J

or

$$\Delta T = \frac{405.28 \text{ J}}{75.312 \text{ J K}^{-1}} = 5.38 \text{ K}$$

Final temperature $= 293 + 5.38$

$$= 298.38 \text{ K}$$

EXAMPLE 4.6 A given sample of nitrogen gas, weighing 2.8 g at 27° C and 20 atm pressure, was allowed to expand isothermally against a constant external pressure of one atmosphere. Calculate ΔU, q and w, assuming ideal behaviour of the gas.

Solution The gas is ideal and it expands isothermally

$$\therefore \quad \Delta U = 0$$

$$\text{or} \quad w = -q$$

$$w = -p_{ex}\,\Delta V = -p_{ex}(V_2 - V_1)$$

$$p_{ex} = 1 \text{ atm},\ n = \frac{2.8}{28} = 0.1 \text{ mol}$$

V_1 and V_2 can be calculated as

$$V_1 = \frac{nRT}{p_1} = \frac{(0.1 \text{ mol})\times(0.082\ l \text{ atm mol}^{-1}\text{K}^{-1})\times(300 \text{ K})}{20 \text{ atm}}$$

$$= 0.123\ l$$

$$V_2 = \frac{nRT}{p_2} = \frac{(0.1 \text{ mol})\times(0.082\ l \text{ atm mol}^{-1}\text{K}^{-1})\times(300 \text{ K})}{1 \text{ atm}}$$

$$= 2.46\ l$$

$$\therefore \quad w = -(1 \text{ atm})\times(2.46-0.123)\ l$$

$$= -\ 2.337\ l \text{ atm}$$

$$= -\ 2.337\times 101.32 \text{ J} \qquad [1\ l \text{ atm} = 101.32 \text{ J}]$$

$$= -0.237 \text{ kJ}$$

Example 4.7(a) Calculate the heat that must be supplied to raise the temperature of 2 kg of water from 25°C to its boiling point at atmospheric pressure. The average specific heat of water in the range 25–100°C is 1.0 cal $g^{-1}K^{-1}$.

(b) How long will a 2 kW heater take to supply this energy ?

Solution Heat required for heating water,

$$q = n\,C_{p,m}\,\Delta T$$

$$n = \frac{2000}{18} = 111.1 \text{ mol}, \qquad \Delta T = 100-25 = 75^\circ$$

Specific heat of water $= 1.0 \text{ cal g}^{-1}\text{ K}^{-1}$.

Molar heat capacity, $C_{p,m} = 1.0\times 18 = 18.0 \text{ cal K}^{-1}\text{ mol}^{-1}$

$$q = (111.1 \text{ mol})\times(18.0 \text{ cal K}^{-1}\text{mol}^{-1})\times 75 \text{ K} = 149.985 \text{ k cal}^*$$

(b) Heat supplied by 2 kW heater $= 2000 \text{ J s}^{-1} = 478.01 \text{ cal s}^{-4}$

Time required to supply 149.985 kcal of heat $= 313.8$ s

or $\qquad = 5$ min 13.8 s

4.10 ENERGY, WORK AND HEAT FOR SOME PROCESSES FOR IDEAL GASES

Isothermal Reversible Process

The internal energy of an ideal gas depends only on temperature, therefore,

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*Alternatively, heat required for heating water can be calculated as = mass × specific heat × ∂T = (2000 g) × (1.0 cal g^{-1} K^{-1}) × 75 K = 150000 cal = 150.0 k cal.

$dU = 0,$ $dH = d(U+pV) = dU+d(RT) = 0$ at constant T,

$$q = -w$$

$$w = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{p_1}{p_2}$$

and $$q = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{p_1}{p_2}$$

Isothermal Isobaric Expansion

At constant T and p_{ex}

$$q = -w$$

$$= \int_{V_1}^{V_2} p_{ex}\, dV = p_{ex}\, \Delta V$$

i.e. all the heat absorbed is used by the system for doing work and hence

$$dU = 0$$

Also, at constant T, $d(pV) = d(nRT) = 0$

$$\therefore \quad dH = 0$$

Reversible Adiabatic Expansion

For adiabatic process,

$$q = 0 \quad \text{or} \quad dU = w$$

or $$dU = \int_{T_1}^{T_2} C_V\, dT$$

$$= C_V\,(T_2 - T_1) \text{ (if } C_V \text{ is taken as constant)}$$

The final temperature T_2 can be calculated from the relations

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

or $$p_1^{1-\gamma}\ T_1^{\gamma} = p_2^{1-\gamma}\ T_2^{\gamma}$$

where $$\gamma = \frac{C_p}{C_V}$$

EXAMPLE 4.8 (SI units) Calculate the amount of work done on 1.5 mol of a perfect gas at 300 K when it is compressed reversibly and isothermally from a pressure of 1.01×10^5 N m^{-2} to 5.05×10^6 N m^{-2}.

Solution For an isothermal reversible process,

Work done on the system, $w = -nRT \ln \dfrac{p_1}{p_2}$

$n = 1.5$ mol, $p_1 = 1.01 \times 10^5$ N m^{-2}, $p_2 = 5.05 \times 10^6$ N m^{-2},
$T = 300$ K, $R = 8.314$ J mol^{-1} K^{-1}

$$w = -(1.5 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K}) \times 2.303 \log \frac{1.01 \times 10^5}{5.05 \times 10^6}$$

$$= 14.639 \times 10^3 \text{ J or } = 14.639 \text{ kJ}$$

$$V_2 = 20\ \text{dm}^3 = 20\times10^{-3}\text{m}^3,\ T = 300\ \text{K}$$
$$a = 0.141\ \text{N m}^4\ \text{mol}^{-2},\ b = 3.91\times10^{-5}\ \text{m}^3\ \text{mol}^{-1}$$

$$w = (8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(300\ \text{K})\times 2.303\log\frac{20\times10^{-3}-3.91\times10^{-5}}{2\times10^{-3}-3.91\times10^{-5}}$$
$$+0.141\ \text{N m}^4\ \text{mol}^{-2}\left[\frac{1}{20\times10^{-3}}-\frac{1}{2\times10^{-3}}\right]\text{m}^{-3}\ \text{mol}$$
$$= 5788.40-63.45$$
$$= 5724.95\ \text{J}$$
$$= 5.725\ \text{kJ}$$

4.11 JOULE-THOMSON EFFECT

The phenomenon of change in temperature when a gas is allowed to expand from high to low pressure through a porous plug or a valve, is known as the *Joules-Thomson effect.* This effect is expressed quantitatively in terms of the Joule-Thomson coefficient, μ_{JT}, which is defined as the rate of change in temperature with pressure when enthalpy remains constant,

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = -\left(\frac{\partial H}{\partial p}\right)_T \Big/ \left(\frac{\partial H}{\partial T}\right)_p = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$
$$= -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial (pV)}{\partial p}\right)_T\right]$$

For ideal gases, $\left(\frac{\partial H}{\partial p}\right)_T$ is zero so that $\mu_{JT} = 0$. If μ_{JT} is positive, then, on expansion, the temperature of the gas decreases and cooling results. This principle is used in the liquefaction of gases. If μ_{JT} is negative and the gas is allowed to expand, the temperature of the gas increases. The sign and magnitude of μ_{JT} depends upon the gas and its conditions. For every gas, there is a temperature where $\mu_{JT}=0$, called the *inversion temperature*. Below this temperature $\mu_{JT} < 0$ and above it $\mu_{JT} > 0$.

EXAMPLE 4.13 (SI units) The Joule-Thomson coefficient for the van der Waals gas equation can be written as

$$\mu_{JT} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

Calculate the inversion temperature for He and H_2 from the following data:

Gas	a (N m^4 mol^{-2})	b (m^3 mol^{-1})
He	3.44×10^{-3}	2.37×10^{-5}
H_2	24.7×10^{-3}	2.66×10^{-5}

Solution Joule-Thomson coefficient

$$\mu_{JT} = \frac{1}{C_p}\left[\frac{2a}{RT} - b\right]$$

At inversion temperature T_i, $\mu_{JT} = 0$

$$\therefore \quad \frac{1}{C_p}\left[\frac{2a}{RT_i} - b\right] = 0$$

$$\text{or} \quad b = \frac{2a}{RT_i}$$

$$\text{or} \quad T_i = \frac{2a}{Rb}$$

Here $R = 8.314 \text{ N m mol}^{-1} \text{ K}^{-1}$

$$T_i(\text{He}) = \frac{2\times(3.44\times10^{-3} \text{ N m}^4 \text{ mol}^{-2})}{(8.314 \text{ N m mol}^{-1} \text{ K}^{-1}) \times (2.37\times10^{-5} \text{ m}^3 \text{ mol}^{-1})}$$
$$= 34.9 \text{ K} = -238.1°\text{C}$$

$$T_i(\text{H}_2) = \frac{2\times(24.7\times10^{-3} \text{ N m}^4 \text{ mol}^{-2})}{(8.314 \text{ N m mol}^{-1} \text{ K}^{-1})\times(2.66\times10^{-5} \text{ m}^3 \text{ mol}^{-1})}$$
$$= 223.4 \text{ K} = -49.6°\text{C}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 4.14 (SI units) One mole of nitrogen, initially at 300 K, is expanded from 10 dm^3 to 20 dm^3. Calculate the maximum work done on the system

(a) by the isothermal expansion
(b) by the adiabatic expansion, assuming ideal behaviour.
(Assume $C_{V,m} = 5/2\, R$)

Solution The maximum work is done in a reversible manner.
(a) when the gas expands isothermally and reversibly

$$w_{max} = nRT \ln \frac{V_2}{V_1}$$

$$n = 1 \text{ mol}, \; T = 273+27 = 300 \text{ K}, \; V_2 = 20 \text{ dm}^3, \; V_1 = 10 \text{ dm}^3$$

$$w_{max} = -(1 \text{ mol})\times(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\times(300 \text{ K})\times2.303 \log \frac{20}{10}$$
$$= -1.729 \text{ kJ}$$

(b) In adiabatic expansion of the gas

$$w = nC_v(T_2 - T_1)$$

$$C_{v,m} = \frac{5}{2}R, \qquad C_{p,m} = \frac{7}{2}R, \qquad T_1 = 300 \text{ K}$$

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

$$\text{or} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 = \left(\frac{10}{20}\right)^{7/5-1} \times 300 \qquad \left(\gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{7}{5}\right)$$
$$= 227.4\ \text{K}$$
$$w = (1\ \text{mol}) \times \left(\frac{5}{2} \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times (227.4-300)\ \text{K}$$
$$= -\ 1.509\ \text{kJ}$$

EXAMPLE 4.15 One mole of an ideal gas at 10 atm pressure is contained in a vessel at 300 K. The gas is expanded till the pressure becomes 2 atm and the temperature reaches 400 K. Calculate the work done on the system and the heat absorbed by it if the change is brought about by the following processes:

(a) The gas is expanded isothermally against a constant external pressure of 2 atm, then heated to the desired temperature at constant volume, and finally expanded till the final state is reached.

(b) The gas is expanded by an isothermal reversible process, then heated to 400 K, and again expanded reversibly till the final state is reached.

(c) The gas is first heated in an isochoric process and then expanded reversibly in an isothermal process.

$C_{v,m}$ of the gas is 5.4 cal mol^{-1}. Show that, for all the processes ΔU is same.

Solution

Path a

(i) The gas is expanded isothermally and the final pressure is 2 atm. Work done on the system,

$$w = -\ p \times \Delta V = -\ p\ (V_2 - V_1)$$
$$V_1 = \frac{nRT_1}{p_1} = \frac{(1\ \text{mol}) \times (0.082\ \text{atm}\ l\ \text{mol}^{-1}\ \text{K}^{-1}) \times (300\ \text{K})}{10\ \text{atm}}$$
$$= 2.46\ l$$
$$V_2 = \frac{nRT_1}{p_2} = \frac{(1\ \text{mol}) \times (0.082\ \text{atm}\ l\ \text{mol}^{-1}\ \text{K}^{-1}) \times (300\ \text{K})}{2\ \text{atm}}$$
$$= 12.3\ l$$
$$\therefore \quad w_1 = -\ (2\ \text{atm}) \times (12.3 - 2.46)\ l = -\ 19.68\ l\ \text{atm.}$$
$$= -\ 19.68 \times 24.218 = -476.6\ \text{cal} \qquad [1\ l\ \text{atm} = 24.218\ \text{cal}]$$

For the expansion of an ideal gas at constant T, $\Delta U = 0$. Hence,

$$q_1 = -\ w_1$$
$$= 476.6\ \text{cal}$$

(ii) The gas is heated from 300 K to 400 K at constant volume. Heat absorbed $q_2 = nC_{v,m}\,(T_2 - T_1) = (1\ \text{mol}) \times (5.4\ \text{cal K}^{-1}\ \text{mol}^{-1})$ $\times (400-300)\ \text{K} = 540\ \text{cal}$

Pressure under these conditions $= \dfrac{2 \times 400}{300} = \dfrac{8}{3}$ atm

(iii) Work done on the system on further expansion to final state

$$w_2 = -\ p\Delta V = -\ p(V_3 - V_2)$$
$$V_2 = 12.3\ l$$

$$V_3 = \frac{nRT}{p_2} = \frac{(1\text{ mol})\times(0.082\text{ atm } l \text{ mol}^{-1}\text{ K}^{-1})\times 400\text{ K}}{2\text{ atm}}$$
$$= 16.4\ l$$

$$w_2 = -(2\text{ atm})\times(16.4-12.3)\ l = -8.2\ l\text{ atm.}$$

or $= -8.2\times 24.218 = -198.6$ cal

and $q_3 = 198.6$ cal

Thus, total work done $w = w_1 + w_2 = -476.6 - 198.6 = -675.2$ cal

and $q = q_1 + q_2 + q_3 = 476.6 + 540 + 198.6 = 1215.2$ cal

$$\Delta U = q + w = 1215.2 - 675.2 = 540\text{ cal}$$

Path b

(i) The gas is expanded isothermally from 10 atm to 2 atm.

$$w_3 = -nRT\ln\frac{V_2}{V_1} = -nRT\ln\frac{p_1}{p_2}$$
$$= -(1\text{ mol})\times(0.082\text{ atm } l\text{ mol}^{-1}\text{ K}^{-1})\times(300\text{ K})\times 2.303\log\frac{10}{2}$$
$$= -39.60\ l\text{ atm} = -39.60\times 24.218 = -959.0\text{ cal}$$
$$q_4 = -w_3 = 959\text{ cal}$$

(ii) When the gas is heated from 300 K to 400 K

Heat absorbed by the system

$$q_5 = nC_{v,m}(T_2 - T_1) = (1\text{ mol})\times(5.4\text{ cal K}^{-1}\text{ mol}^{-1})\times(400-300)\text{ K}$$
$$= 540\text{ cal}$$

Pressure under these conditions $= \dfrac{(2\text{ atm})\times(400\text{ K})}{300\text{ K}} = \dfrac{8}{3}$ atm

(iii) Work done on the system in isothermal reversible expansion

$$w_4 = -nRT\ln\frac{p_1}{p_2} = -(1\text{ mol})\times(0.082\text{ atm } l\text{ mol}^{-1}\text{ K}^{-1})$$
$$\times(400\text{ K})\times 2.303\log\frac{8/3}{2}$$
$$= -9.43\ l\text{ atm} = -228.4\text{ cal}$$

and $q_6 = -w_4 = 228.4$ cal

Total work done in path b

$$w = w_3 + w_4 = -959.0 - 228.4 = -1187.4\text{ cal}$$
$$q = q_4 + q_5 + q_6 = 959.0 + 540 + 228.4 = 1727.4\text{ cal}$$
$$\Delta U = q + w = 1727.4 - 1187.4 = 540\text{ cal}$$

Path c

(i) The gas is heated at constant volume,

$$q = nC_{v,m}(T_2 - T_1) = (1\text{ mol})\times(5.4\text{ cal K}^{-1}\text{ mol}^{-1})\times(400-300)\text{ K}$$
$$= 540\text{ cal}$$

Pressure under these conditions $= 10\times\dfrac{400}{300} = \dfrac{40}{3}$ atm

(ii) The gas is expanded from 40/3 atm to 2 atm

$$w_5 = -nRT\ln\frac{p_1}{p_2} = (1\text{ mol})\times(0.082\text{ atm } l\text{ mol}^{-1}\text{ K}^{-1})\times(400\text{ K})$$
$$\times 2.303\times\log\frac{40}{3}\Big/2$$

$=-62.24\ l\ \text{atm} = -1507.3\ \text{cal}$

and $q_8 = -w_5 = 1507.3$ cal

Total work done in path c

$w = w_5 = -1507.3$ cal

$q = q_7 + q_8 = 540 + 1507.3 = 2047.3$ cal

$\Delta U = q + w = 2047.3 - 1507.3 = 540$ cal

Thus, it is clear that q and w are different in all three cases (as these depend on the path) but ΔU is the same.

Example 4.16 Calculate the values of ΔH and ΔU for the reversible isothermal evaporation of 180 g of water at 100°C. Assume water vapour behaves as an ideal gas (latent heat of evaporation of water $= 539.7$ cal K^{-1} g^{-1}).

Solution Since ΔH is the heat absorbed at constant pressure, in evaporating 180 g of water,

$$\Delta H = 180 \times 539.7 = 97146 \text{ cal}$$
$$= 97.146 \text{ kcal}$$
$$\Delta H = \Delta U + p\Delta V$$

The volume of liquid is negligible compared to that of vapour and water vapour is assumed to behave like ideal gas:

$$p\Delta V = pV_{\text{vap}} = nRT$$
$$\Delta H = \Delta U + nRT$$
$$n = \frac{180}{18} = 10 \text{ mol},\ T = 273 + 100 = 373 \text{ K},\ R = 1.98 \text{ cal mol}^{-1} \text{ K}^{-1}$$
$$\Delta U = \Delta H - nRT$$
$$= 97146 - 10 \times 1.98 \times 373$$
$$= 89761 \text{ cal or } 89.761 \text{ kcal}$$

Example 4.17 (SI units) A coloured TV of 600 W is switched on in a room of dimensions $5 \times 4 \times 3$ m. Estimate the increase in temperature of the room after 15 min, if the average specific heat of air at room temperature and 1 atm is 0.71 J $g^{-1}K^{-1}$ and the heat capacity of the four walls and the roof is 50×10^3 J K^{-1} (Density of air ≈ 1.22 kg m^{-3}).

Solution

Heat given out by TV in 15 min $= (600 \text{ J s}^{-1}) \times (60 \times 15 \text{ s})$
$= 54 \times 10^4$ J

Volume of the room $= 5 \times 4 \times 3 = 60\ \text{m}^3$

Mass of air in the room $= (60\ \text{m}^3) \times (1.22\ \text{kg m}^{-3}) = 73.2$ kg

Heat capacity of air in the room $= (0.71\ \text{J g}^{-1}\ \text{K}^{-1})\ (73.2 \times 10^3\ \text{g})$
$= 51.972 \times 10^3\ \text{J K}^{-1}$

Heat capacity of the four walls and the roof $= 50 \times 10^3\ \text{J K}^{-1}$

Total heat capacity $= (51.972 \times 10^3 + 50 \times 10^3)\ \text{J K}^{-1}$
$= 101.972 \times 10^3\ \text{J K}^{-1}$

Now,

Heat given out by TV = Heat capacity × ΔT

$$54\times10^4 \text{ J} = 101.972\times10^3 \text{ J K}^{-1}\times\Delta T$$

or $$\Delta T = \frac{54\times10^4}{101.972\times10^3} = 5.3 \text{ K}$$

Increase in temperature of the room = 5.3 K

EXAMPLE 4.18 A gas obeys the van der Waals equation. Derive the relation for work done if the gas expands isothermally and reversibly from volume V_1 to V_2.

Solution The work done during expansion from volume V_1 to V_2

$$w = -\int_{V_1}^{V_2} p dV$$

The van der Waals equation for one mole of gas is

$$\left(p+\frac{a}{V^2}\right)(V-b) = RT$$

or $$p = \frac{RT}{V-b}-\frac{a}{V^2}$$

Substituting the value of p

$$w = -\int_{V_1}^{V_2}\left[\frac{RT}{V-b}-\frac{a}{V^2}\right]dV$$

$$= -\left[RT\ln(V-b)+\frac{a}{V}\right]_{V_1}^{V_2}$$

$$= -RT\ln\frac{V_2-b}{V_1-b}+a\left[\frac{1}{V_2}-\frac{1}{V_1}\right]$$

EXAMPLE 4.19 Prove that, for any substance,

$$C_{p,m}-C_{v,m} = \left[p+\left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

Further show that it simplifies to

$C_{p,m} - C_{v,m} = R$ for an ideal gas.

Solution $C_{p,m}$ and $C_{v,m}$ are defined as

$$C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p \text{ and } C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v$$

$$C_{p,m}-C_{v,m} = \left(\frac{\partial H}{\partial T}\right)_p-\left(\frac{\partial U}{\partial T}\right)_v \qquad (H = U+pV)$$

$$= \left[\frac{\partial(U+pV)}{\partial T}\right]_p-\left(\frac{\partial U}{\partial T}\right)_v$$

$$= \left(\frac{\partial U}{\partial T}\right)_p+p\left(\frac{\partial V}{\partial T}\right)_p-\left(\frac{\partial U}{\partial T}\right)_v \qquad (1)$$

Since
$$U = f(T, V)$$
$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial V}\right)_T . dV$$
$$\therefore \quad \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p \tag{2}$$

Substituting Eq. (2) in Eq. (1)

$$C_{p,m} - C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p - \left(\frac{\partial U}{\partial T}\right)_v$$
$$= p\left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$
$$= \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$$

For ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_{p,m} - C_{v,m} = p\left(\frac{\partial V}{\partial T}\right)_p$$

Now
$$pV = RT \quad \text{or} \quad V = \frac{RT}{p}$$
$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p}$$

So that $C_{p,m} - C_{v,m} = \frac{p \times R}{p} = R$

$$C_{p,m} - C_{v,m} = R \text{ for an ideal gas}$$

EXAMPLE 4.20 The Joule-Thomson coefficient is defined as

$$\mu_{\text{JT}} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

Using this, derive the equation

$$\mu_{\text{JT}} = -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T + \frac{\partial pV}{\partial p}\right]$$

Solution

$$\mu_{\text{JT}} = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

But
$$H = U + pV$$
$$\mu_{\text{JT}} = -\frac{1}{C_p}\left[\frac{\partial(U+pV)}{\partial p}\right]_T$$
$$= -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial p}\right)_T + \left(\frac{\partial pV}{\partial p}\right)_T\right]$$
$$= -\frac{1}{C_p}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial p}\right)_T + \left(\frac{\partial pV}{\partial p}\right)_T\right]$$

QUESTIONS

Numerical Problems

4.1 (SI units) Calculate the amount of work done by 0.5 mol of an ideal gas at 300 K when it expands isothermally and reversibly from 1 dm^3 to 10 dm^3.

4.2 (SI units) One mole of an ideal gas at 300 K was compressed reversibly from 5 m^3 to a final volume of 200 m^3. Calculate the work done on it.

4.3 Calculate the work done to compress 0.5 mol of oxygen at 300 K from a pressure of 1 atm to a pressure of 100 atm.

4.4 (SI units) A quantity of nitrogen weighing 0.056 kg expands isothermally at 400 K reversibly and isothermally, from 15 dm^3 to 45 dm^3. Determine q, w, ΔU and ΔH for the system, assuming ideal behaviour of nitrogen.

4.5 (SI units) Calculate the amount of work done on 2.5 mol of a perfect gas at 300 K when it is compressed reversibly and isothermally from a pressure of 1.0×10^2 kPa to 5.0×10^3 kPa.

4.6 (SI units) One mole of an ideal gas absorbs 500 J of heat and expands from 2 dm^3 to 6 dm^3 in vacuum. Calculate q, w and ΔU.

4.7 (SI units) If 2.5 moles of an ideal gas at a certain temperature are allowed to expand isothermally and reversibly, from an initial volume of 2 dm^3 to 20 dm^3, then the work done on the gas is -16.5 kJ. Calculate the temperature of the gas.

4.8 Two moles of a gas which behaves ideally are allowed to expand at 0°C against a confining pressure in such a way that, all the time, it is infinitesimally less than the gas pressure. Calculate the work done and heat absorbed in this process if the initial and final pressures are 20 atm and 2 atm, respectively.

4.9 A quantity of 0.5 mol of an ideal gas, initially at a pressure of 20 atm and 300 K, is allowed to expand isothermally until its final pressure is 2 atm. Calculate the work done by it if the expansion is carried out (i) against vacuum, (ii) against a constant external pressure of 2 atm and (iii) reversibly. In which of these processes maximum work will be done.

4.10 One mole of an ideal gas is heated at constant pressure (1 atm), from 0°C to 120°C. (a) Calculate the work done in this process. (b) If the gases were expanded isothermally and reversibly at 0°C, from 1 atm to some other pressure p, what would be the value of p if the work done is equal to that in part (a) ?

4.11 One mole of an ideal gas, with $C_{v,m} = 12.47$ J mol^{-1} K^{-1}, is heated reversibly, at a constant pressure of 760 torr, from -25°C to 25°C. Calculate ΔU and ΔH.

4.12 (SI units) For a certain gas, $C_{v,m} = 28.3$ J mol^{-1} K^{-1}. When 10 mol of the gas are heated at 298 K to temperature T°K, ΔH of the process has been found to be 1.831 J. Calculate T.

4.13 Five moles of an ideal monoatomic gas is compressed reversibly and adiabatically, from a volume of 80 dm^3 at 1 atm to a pressure of 20 atm. Calculate the final temperature and volume of the gas.

4.14 When 5 J of heat is transferred to 1 g of water at 20°C, its temperature rises to 21.2°C. What is the molar heat capacity of water in this temperature range?

4.15 For helium gas, $\gamma = 1.66$. Calculate the decrease in temperature if helium at 25°C is expanded adiabatically to triple its volume.

4.16 One mole of an ideal monoatomic gas, initially at a pressure of 20 atm and 300 K, is allowed to expand reversibly and adiabatically until its final pressure is 2 atm. How much work is done in this process by the gas ?

4.17 (SI units) Calculate q, w and ΔU for the adiabatic reversible compression of 1 mol of a monoatomic gas from 25 dm^3 to 5 dm^3. The initial temperature of the gas is 300 K.

4.18 Two moles of an ideal gas ($C_{v,m} = 3.0$ cal K^{-1} mol^{-1}) are at 20 atm and 300 K. Calculate and compare the work done if the gas is allowed to expand to 2 atm (i) reversibly isothermally and (ii) reversibly adiabatically.

4.19 (SI units) Calculate the maximum work obtainable by (a) isothermal expansion and (b) adiabatic expansion of 2 moles of nitrogen (assumed ideal), initially at 300 K, from 2 dm^3 to 10 dm^3 ($C_{v,m}$ for the gas is $5/2\,R$).

4.20 Calculate the work done when one mole of oxygen at 37°C expands isothermally and reversibly from 5 dm^3 to 20 dm^3. The van der Waals parameters are $a = 1.36$ dm^6 atm mol^{-2} and $b = 31.8\times10^{-3}$ dm^3 mol^{-1}.

4.21 The Joule-Thomson coefficient for a van der Waals gas is

$$\mu_{JT} = \frac{2a/RT - b}{C_p}$$

Calculate the inversion temperature for CH$_4$; $a = 2.25$ atm dm^6 mol^{-2} and $b = 0.043$ dm^3 mol^{-1}.

4.22 The Joule-Thomson coefficient for a van der Waals gas is

$$\mu_{JT} = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right).$$

Calculate ΔH for the isothermal compression of one mole of nitrogen at 300 K from a pressure of 1 to 100 atm ($a = 1.35$ atm l^2 mol^{-2}, $b = 0.038$ l mol^{-1}).

4.23 Oxygen is allowed to expand adiabatically through a porous plug, in a Joule-Thomson experiment, from 100 atm to the final pressure of 1 atm. The temperature of the gas drops from 25°C to −11°C. Calculate the Joule-Thomson coefficient.

4.24 The Joule-Thomson coefficient of N$_2$ is + 0.25 K atm^{-1}. Calculate the final temperature of the gas if 2 mol of N$_2$, initially at 20 atm and 0°C, are allowed to expand adiabatically through a porous plug until the final pressure is 1 atm. (Assume the Joule-Thomson coefficient to be independent of temperature).

4.25 A water bath containing 50 kg of water is to be heated from 20°C to 50°C. How long will a 2 kW immersion heater take to heat water ? The specific heat of water in this range of temperature is 1 cal g^{-1} K^{-1}.

4.26 Calculate the number of calories of heat required to warm a copper pan filled with 1 kg of water, from 25 to 60°C, if the pan weighs 200 g. The average molar heat capacity, at constant pressure of copper = 5.85 cal K^{-1} mol^{-1} and average molar heat capacity $C_{p,m}$ of water = 18 cal K^{-1} mol^{-1} (At mass of Cu = 63.5).

4.27 (SI units) How much time will a 2 kW room heater take to heat an empty room with the dimensions 5 × 4 × 4 m, by 10 K, assuming no heat is lost ? For air, average specific heat = 0.72 J K^{-1} g^{-1}; density = 1.22 kg m^{-3}, molecular mass = 29.

4.28 A real gas obeys the van der Waals equation of state. Calculate the changes q, w and ΔU for n moles of the gas if it expands isothermally and reversibly.

4.29 Show that

(i) $C_{p,m} - C_{v,m} = p\left[1 + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_p$

(ii) $C_{p,m}\ C_{v,m} = -T\left(\frac{\partial V}{\partial T}\right)_p^2 \Big/ \left(\frac{\partial V}{\partial p}\right)_T$

(iii) $\mu_{JT} = \frac{1}{C_p}\left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]$

4.30 Show that the work involved in the adiabatic reversible expansion of one mole of an ideal gas is given by the relation :

$$w = -C_{v,m}\,T_1\left[1-\left(\frac{p_2}{p_1}\right)^{R/C_{p,m}}\right]$$

If $C_{v,m}$ and $C_{p,m}$ are independent of temperature.

QUIZ QUESTIONS

Type A: Multiple Choice

4.31 A system which can exchange matter as well as energy with its surroundings is said to be a/an

(a) isolated system
(b) open system
(c) inert system
(d) closed system

4.32 A closed system is one which can exchange, with surroundings,

(a) matter as well as energy
(b) matter but not energy
(c) energy but not matter
(d) neither energy nor matter

4.33 Any property whose magnitude is independent of the amount of substance present is called a/an

(a) colligative property
(b) intensive property
(c) extensive property
(d) none of the above

4.34 An example of an extensive property is

(a) temperature
(b) pressure
(c) molar volume
(d) enthalpy

4.35 Which of the following is not an intensive property ?

(a) entropy
(b) temperature
(c) chemical potential
(d) molar volume

4.36 A process in which no heat enters or leaves the system is called

(a) isothermal
(b) isobaric
(c) adiabatic
(d) isochoric

4.37 In an isochoric process

(a) volume remains constant
(b) pressure remains constant
(c) temperature remains constant
(d) energy remains constant

4.38 ΔH and ΔU are related as

(a) $\Delta U = \Delta H + p\,\Delta V$
(b) $\Delta H = \Delta U - p\,\Delta V$

(c) $\Delta U = p\Delta V - \Delta H$
(d) $\Delta H = \Delta U + \Delta\,(pV)$

4.39 Enthalpy H is defined as
(a) $H = \frac{U}{pV}$
(b) $H = U + pV$
(c) $H = U\,(p + V)$
(d) $H = U - pV$

4.40 The difference between ΔH and ΔU at constant volume is equal to
(a) R
(b) $p\Delta V$
(c) $V\Delta p$
(d) $\frac{3}{2}R$

4.41 For an adiabatic process
(a) $q = +w$
(b) $\Delta U < w$
(c) $\Delta U \geqslant w$
(d) $q = 0$

4.42 When a sample of an ideal gas is allowed to expand reversibly and isothermally in vacuum,
(a) $w = 0, \Delta U = q > 0$
(b) $\Delta U = 0, q = w > 0$
(c) $\Delta U = 0, q = -p\Delta V$
(d) $\Delta U = q = w = 0$

4.43 Which of the following is not a state function ?
(a) $q + w$
(b) $\frac{H}{T}$
(c) $U + pV$
(d) $\frac{q}{w}$

4.44 Which of the following is always true for the adiabatic expansion of a gas (real or ideal) ?
(a) temperature rises
(b) $\Delta U = 0$
(c) $q = 0$
(d) $w = 0$

4.45 Molar heat capacities $C_{p,m}$ and $C_{v,m}$ are expressed as
(a) $C_{p,m} = \left(\frac{\partial U}{\partial T}\right)_p \quad C_{v,m} = \left(\frac{\partial H}{\partial T}\right)_v$
(b) $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p \quad C_{v,m} = \left(\frac{\partial H}{\partial U}\right)_v$
(c) $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p + \left(\frac{\partial T}{\partial H}\right)_p \quad C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v + \left(\frac{\partial T}{\partial U}\right)_v$
(d) $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p \quad C_{v,m} = \left(\frac{\partial U}{\partial T}\right)_v$

4.46 The difference between molar heat capacity at constant pressure ($C_{p,m}$) and at constant volume ($C_{v,m}$) for an ideal gas is equal to
(a) $\frac{\Delta H}{\Delta U}$
(b) R
(c) $p\Delta V$
(d) zero

4.47 In an adiabatic expansion of an ideal gas in vacuum
(a) $\Delta H = 0$

(b) $\Delta U = 0$
(c) $\Delta H = \Delta U$
(d) $\Delta H = \Delta U + RT$

4.48 The Joule-Thomson coefficient is defined as
(a) $\left(\frac{\partial T}{\partial P}\right)_H$
(b) $\left(\frac{\partial T}{\partial H}\right)_p$
(c) $\left(\frac{\partial H}{\partial T}\right)_p$
(d) $\left(\frac{\partial p}{\partial T}\right)_p$

4.49 For an ideal gas
(a) $\left(\frac{\partial P}{\partial T}\right)_v = 0$
(b) $\left(\frac{\partial U}{\partial T}\right)_p = 0$
(c) $\left(\frac{\partial U}{\partial V}\right)_T = 0$
(d) $\left(\frac{\partial U}{\partial T}\right)_v = 0$

4.50 The temperature below which a gas becomes cooler on expansion is called the
(a) critical temperature
(b) reduced temperature
(c) transition temperature
(d) inversion temperature

4.51 The Joule-Thomson coefficient of an ideal gas is zero because
(a) the molecules move in straight lines
(b) the volume of molecules is negligible
(c) there are no attractive forces between molecules
(d) the molecules make elastic collisions

4.52 At room temperature, the effect produced by the Joule-Thomson expansion of H_2 and He is
(a) cooling
(b) heating
(c) neither cooling nor heating
(d) liquefaction

4.53 During the reversible expansion of an ideal gas from volume V_1 to V_2, at constant temperature T, the work done on the gas is
(a) $-nRT \ln \frac{V_2}{V_1}$
(b) $\frac{nRT}{2.303} \log \frac{V_1}{V_2}$
(c) $-\frac{nR}{T} \ln \frac{V_1}{V_2}$
(d) $-nRT\,(V_2 - V_1)$

4.54 If heat absorbed by the system is q, work done on the system is w, and change in internal energy is ΔU, then the first law of thermodynamics may be expressed as
(a) $\Delta U + q + w = 0$

(b) $\Delta U = q + w$

(c) $q - w = \Delta U$

(d) $\Delta U = \dfrac{q}{w}$

4.55 Molar heat capacity at constant pressure may be expressed as

(a) $\left(\dfrac{\partial U}{\partial T}\right)_v$

(b) $\left(\dfrac{\partial H}{\partial T}\right)_p$

(c) $\left(\dfrac{\partial H}{\partial T}\right)_v$

(d) $\left(\dfrac{\partial U}{\partial T}\right)_v + \left(\dfrac{\partial H}{\partial T}\right)_p$

Type B: Multiple Choice (Numerical Problems)

4.56 The work done by the system in a cyclic process involving one mole of an ideal monoatomic gas is −50 kJ/cycle. The heat absorbed by the system per cycle is

(a) zero
(b) 50 kJ
(c) −50 kJ
(d) 250 kJ

4.57 The work done by the system in the conversion of 1 mol of water at 100°C and 760 torr to steam is −3.1 kJ. Calculate ΔU for the conversion (latent heat of vaporisation of water is 40.65 kJ mol^{-1})

(a) 43.75 kJ
(b) 101.35 kJ
(c) 37.55 kJ
(d) −40.65 kJ

4.58 One mole of an ideal gas ($C_{v,m} = 5$ cal K^{-1} mol^{-1}), initially at STP, is heated at constant volume to twice the initial temperature. For this process w and q are (assume $R \approx 2$ cal).

(a) $w = 0$, $q = 1.365$ kcal
(b) $w = -1.365$ kcal, $q = 1.365$ kcal
(c) $w = 0$, $q = 1.911$ kcal
(d) $w = 0$, $q = 0$

4.59 An ideal gas expands from 10^{-3} m^3 to 10^{-2} m^3 at 300 K, against a constant pressure of 10^5 N m^{-2}. The work done on it is

(a) −0.9 kJ
(b) −900 kJ
(c) 270 kJ
(d) −270 kJ

4.60 A gas absorbs 400 J of heat and expands by 2×10^{-3} m^3 against a constant pressure of 1×10^5 N m^{-2}. The change in internal energy of gas is

(a) zero
(b) 200 J
(c) −600 J
(d) −200 J

4.61 One mole of a gas absorbs 200 J of heat at constant volume. Its temperature rises from 298 K to 308 K. The change in internal energy (ΔU) is

(a) 200 J

(b) −200 J

(c) $200 \times \dfrac{308}{298}$ J

(d) $200 \times \dfrac{298}{308}$ J

4.62 Calculate the work done on the system if one mole of an ideal gas at 500 K is compressed isothermally and reversibly to one-tenth of its original volume ($R \approx 2$ cal)

(a) 500 kcal
(b) 1.151 kcal
(c) −23.03 kcal
(d) 2.303 kcal

4.63 How many calories are required to heat 40 g of argon from 40 to 100°C at constant volume ? ($R = 2$ cal mol^{-1} K^{-1})
(a) 180 cal (b) 7.2 kcal
(c) 40 cal (d) 1800 cal

4.64 When 4.184 J of heat is transferred to 1 g of water at 20°C its temperature rises to 21°C. The molar heat capacity at this temperature is
(a) 18 J K^{-1} mol^{-1}
(b) $\frac{18}{4.184}$ J K^{-1} mol^{-1}
(c) 75.4 J K^{-1} mol^{-1}
(d) 4.184 J K^{-1} mol^{-1}

4.65 The approximate heat necessary to raise the temperature of 92 g of ethyl alcohol from 25 to 35°C at 1 atm pressure ($C_{p,m} = 26.8$ cal °C^{-1} mol^{-1}) is
(a) 268 cal mol^{-1}
(b) 134 cal mol^{-1}
(c) 67 cal mol^{-1}
(d) 536 cal mol^{-1}

4.66 The time taken by a 1 kW heater to heat 1.8 kg of water from 25° to 35°C ($C_{p,m}$ of water in this temperature range $= 75.5$ J K^{-1} mol^{-1}) is
(a) 75.5 min
(b) $75.5 \times 1.8 \times 10^3$ s
(c) 1 min 15.5 s
(d) 755 s

4.67 Two moles of an ideal monoatomic gas are allowed to expand adiabatically and reversibly from 300 K to 200 K. The work done on the system is ($C_{v,m} = 12.5$ J K^{-1} mol^{-1})
(a) −12.5 kJ (b) − 2.5 kJ
(c) −6.25 kJ (d) 50.0 kJ

4.68 For the reversible isothermal expansion of one mole of an ideal gas at 300 K, from a volume of 10 dm^3 to 20 dm^3, ΔH is
(a) 1.73 kJ
(b) −1.73 kJ
(c) 3.46 kJ
(d) zero

4.69 One mole of a gas absorbs 500 J of heat at constant volume. Its temperature is raised from 25° to 35°C. The values of q, w and ΔU are
(a) $\Delta U = 0$, $q = w = 500$ J
(b) $\Delta U = q = 500$ J, $w = 0$
(c) $\Delta U = w = 500$ J, $q = 0$
(d) $\Delta U = 0$, $q = 500$ J, $w = -500$ J

4.70 The heat capacity of air at room temperature and 1 atm pressure is 21 J K^{-1} mol^{-1}. How much heat is required to heat a room through 1°K at room temperature (Assume air present in the room = 290 kg and average mol mass of air = 29) ?
(a) 210 kJ (b) 2100 kJ
(c) 210 J (d) 420 kJ

Type C: True or False

4.71 The numerical value of change in internal energy is independent of the manner in which the change has occurred.

4.72 Change in enthalpy is always larger than change in internal energy.

4.73 The temperature below which a gas becomes cooler on expansion is called inversion temperature.
4.74 The maximum work can be extracted from a system in a reversible manner.
4.75 Temperature remains constant in adiabatic as well as isothermal processes.
4.76 Energy is a function of state while work and heat are not.
4.77 There is no theoretical proof for the first law of thermodynamics, it is based on human experience alone.
4.78 During Joule-Thomson expansion, temperature decreases for all gases above the inversion temperature.
4.79 Joule-Thomson coefficient is zero for an ideal gas.
4.80 If a process involves contraction of a gas, then work done on it is negative.
4.81 Temperature, mole fraction and chemical potential are all intensive properties.
4.82 For an isothermal expansion of an ideal gas $\Delta U = 0$ but $\Delta H > 0$.
4.83 dU is an exact differential while tq and tw are inexact differentials.
4.84 Work and heat are meaningfull only when a system undergoes a process.
4.85 In a cyclic process $\Delta U = 0$

Type D: Fill in the Blanks

4.86 A process in which no heat enters or leaves the system is called................. process.
4.87 In an.................process, the pressure of the system remains constant.
4.88 A system which is completely uniform throughout is called..............system.
4.89 The temperature at which the Joule-Thomson coefficient changes sign is called................. .
4.90 The property whose value in the system as a whole is the sum of the values for different parts of the system is called.................property.
4.91 For any constant-pressure reversible process, the increase in enthalpy is equal to................. .
4.92 For systems in condensed phases at constant pressure, the enthalpy change is................energy change.
4.93 The heat capacity of a given amount of substance is given by the product of number of moles and................. .
4.94 Besides internal energy, a system may also have................and.................... energies.
4.95 When work has been done on the system, w is................., and when heat has been flown out of the system, q is................. .

ANSWERS

Numerical Problems

4.1 2.872 kJ *4.2* 2285.8 J *4.3* 5.744 kJ *4.4* $q = 7308.4$ J, $w = -7308.4$ J, $\Delta U = 0$, $\Delta H = 0$ *4.5* 14.639 kJ *4.6* During expansion in vacuum, $w = 0$, $q = 500$ J, $\Delta U = 500$ J *4.7* 344.7 K *4.8* $q = 5.227$ kJ, $w = -5.227$ kJ *4.9* (i) 0 (ii) -1121.7 J (iii) -2872.1 J, Maximum work will be done in (iii) *4.10* (a) 238.44 cal (b) 0.6443 atm *4.11* 623.5 J, 1039.2 J *4.12* 50°C *4.13* 646.34 K, 13.25 dm^3 *4.14* 75.76 J mol^{-1} deg^{-1} *4.15* 153.7 *4.16* -2250.8 J *4.17* $q=0$, $w=7080.5$ J, $\Delta U=7080.5$ J *4.18* (i) -11.49 kJ (ii) -4.50 kJ *4.19* (a) -8.03 kJ (b) -5.92 kJ *4.20* -3.456 kJ *4.21* 1276.2 K *4.22* 719.8 J mol^{-1} *4.23* $+0.36$ *4.24* -4.94°C *4.25* 52 min 18 s *4 26* 35.645 kcal *4.27* 5 min 51 s

Quiz Questions

4.31 (b) *4.32* (c) *4.33* (b) *4.34* (d) *4.35* (a) *4.36* (c) *4.37* (a) *4.38* (d) *4.39* (b) *4.40* (c) *4.41* (d) *4.42* (d) For isothermal expansion in vacuum, $w = 0 = q$ and $\Delta U = 0$ (isothermal) *4.43* (d) *4.44* (c) *4.45* (d) *4.46* (b) *4.47* (b) *4.48* (a) *4.49* (c) *4.50* (d) *4.51* (c) *4.52* (b) : In Joule-Thomson expansion, cooling occurs below the inversion temperature, and heating above the inversion temperature. For H_2 and He, inversion temperature is very low (−80°C and −173°C respectively). *4.53* (a) *4.54* (b) *4.55* (d) *4.56* (c) *4.57* (c) *4.58* (a) *4.59* (a) *4.60* (b) *4.61* (a) *4.62* (d) *4.63* (a) *4.64* (c) *4.65* (d) *4.66* (c) *4.67* (b) *4.68* (d) *4.69* (b) *4.70* (a) *4.71* True *4.72* False : $\Delta H = \Delta U + p\Delta V$; if system expands ΔV is +ve and $\Delta H > \Delta U$. If system contracts ΔV is −ve and $\Delta H < \Delta U$. If system does not undergo volume change $\Delta V = 0$ and $\Delta H = \Delta U$ *4.73* True *4.74* True *4.75* False : Temperature is constant only for isothermal process *4.76* True *4.77* True *4.78* False *4.79* True *4.80* False *4.81* True *4.82* False *4.83* True *4.84* True *4.85* True *4.86* an adiabatic *4.87* isobaric *4.88* homogeneous *4.89* inversion temperature *4.90* extensive *4.91* heat absorbed at constant pressure *4.92* nearly equal *4.93* molar heat capacity *4.94* potential, kinetic *4.95* +ve, −ve

5

Thermochemistry

Chemical reactions are normally accompanied by energy changes. These energy changes may occur in the form of heat, light or mechanical work. Sometimes, the energy changes associated with chemical reactions are more important than the products of the reaction, e.g. burning of coal and other fuels. The branch of science which deals with heat changes during chemical reactions is called *thermochemistry*. This chapter deals with the heats of various types of reactions and their temperature dependence.

5.1 ENERGY CHANGES IN CHEMICAL REACTIONS

A chemical reaction is generally accompanied by evolution or absorption of heat which may be written as

$$\mathrm{A} + \mathrm{B} = \mathrm{C} + \mathrm{D} + q \text{ (heat)}$$

If the reaction occurs at constant volume, then heat absorbed

$$q_v = \Delta U$$

If the reaction occurs at constant pressure, then heat absorbed

$$q_p = \Delta H$$

ΔU and ΔH are called the energy change and enthalpy change of a reaction and are related by the equation (assuming ideal gas behaviour)

$$\Delta H = \Delta U + \Delta nRT$$

where $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

$\Delta U = U_{\text{products}} - U_{\text{reactants}}$

$\Delta n =$ Number of moles of gaseous products $-$ Number of moles of gaseous reactants

EXAMPLE 5.1 The enthalpy changes for the following reactions, at 25°C and 1 atm, are given below:

(a) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H^\circ = -1368$ kJ

(b) $CH_3COOH(l) + 2O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l) \quad \Delta H^\circ = -874$ kJ

Calculate the energy changes for these reactions.

Solution ΔH and ΔU are related as

$$\Delta H = \Delta U + \Delta nRT \quad \text{or} \quad \Delta U = \Delta H - \Delta nRT$$

(a) $\Delta H = -1368$ kJ, $\Delta n = 2-3 = -1$ mol, $T = 298$ K

$R = 8.314$ J mol^{-1}K^{-1} or 8.314×10^{-3} kJ mol^{-1} K^{-1}

$$\Delta U = -1368 \text{ kJ} - (-1 \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$$
$$= -1365.5 \text{ kJ}$$

(b) $\Delta H = -874$ kJ, $\Delta n = 2-2 = 0$

$\Delta U = \Delta H = -874$ kJ

Temperature Dependence of ΔH and ΔU (Kirchhoff's Equation)

For a given reaction ΔH and ΔU generally vary with temperature. If ΔH_2 and ΔH_1 are the enthalpies of the reaction at temperatures T_2 and T_1 respectively and ΔC_p is the difference between the sums of heat capacities of the products and the reactants at a given temperature T, then

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \, dT$$

This is called *Kirchhoff's equation*. The following special cases are of interest:

(i) If ΔC_p is zero, then $\Delta H_2 = \Delta H_1$
i.e. enthalpy of reaction does not change with temperature.

(ii) If ΔC_p is constant, then $\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1)$
i.e. ΔH changes linearly with increase of temperature.

(iii) If ΔC_p changes with temperature, then the equation has to be integrated by expressing ΔC_p as a function of temperature.

In a similar way,

$$\Delta U_2 = \Delta U_1 + \int_{T_1}^{T_2} \Delta C_v \, dT$$

It is generally possible to write C_p and C_v as:

$$C_p = a + bT + cT^2 + \ldots$$

and

$$C_V = a' + b'T + c'T^2 + \ldots$$

where $a, b, c, \ldots$ and $a', b', c', \ldots$ are constants depending upon the nature of the substances.

Example 5.2 (SI units) The molar heat capacities for $H_2O(s)$ and $H_2O(l)$ are 37.7 J mol^{-1} K^{-1} and 75.3 J mol^{-1} K^{-1} respectively. The enthalpy of fusion of ice at −10°C is 5.627 kJ mol^{-1}. Calculate the enthalpy of fusion of ice at 0°C assuming that molar heat capacities are independent of temperature in this range.

Solution According to Kirchhoff's equation:

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \, dT$$

or
$$\Delta H(273) = \Delta H\,(263) + \int_{263}^{273} \Delta C_p\, dT$$

$$\begin{aligned}
\Delta H(263) &= 5.627\times10^3 \text{ J mol}^{-1}\\
\Delta C_p &= (75.3-37.7) = 37.6 \text{ J mol}^{-1}\text{ K}^{-1}\\
\Delta H(273) &= 5627 \text{ J mol}^{-1}+(37.6 \text{ J mol}^{-1}\text{ K}^{-1})\times(273-263)\text{ K}\\
&= 6003 \text{ J mol}^{-1}\\
&=6.003 \text{ kJ mol}^{-1}
\end{aligned}$$

EXAMPLE 5.3 (SI units) For a hypothetical reaction

$$\text{A} + \text{B} \longrightarrow \text{AB}$$

ΔC_p is given by the equation $40.0+5.0\times10^{-3}T$ J K^{-1} in the temperature range 300-600 K. The enthalpy of the reaction at 300 K is -25.0 kJ. Calculate the enthalpy of the reaction at 450 K.

Solution According to Kirchhoff's equation

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p\, dT$$

$$\begin{aligned}
\Delta H_1 \quad \text{or} \quad \Delta H(300) &=-\ 25 \text{ kJ} =-\ 25000 \text{ J},\\
\Delta C_p &= (40+5\times10^{-3}T) \text{ J K}^{-1}
\end{aligned}$$

$$\begin{aligned}
\therefore\ \Delta H_2 \text{ or } \Delta H(450) &=-\ 25000 \text{ J}+\int_{300}^{450} (40+5\times10^{-3}\ T)\, dT\\
&=-\ 25000+40(450-300)+5\times10^{-3}\frac{(450^2-300^2)}{2}\\
&=-\ 18718.8 \text{ J}\\
&=-\ 18.72 \text{ kJ}
\end{aligned}$$

EXAMPLE 5.4 For the reaction at 25°C

$$\text{Fe}_2\text{O}_3\text{(s)} + 3\text{H}_2\text{(g)} \longrightarrow 2\text{Fe(s)} + 3\text{H}_2\text{O(l)}$$

$\Delta H^\circ =-\ 35.1$ kJ. Calculate the temperature at which $\Delta H=-28.5$ kJ for the same reaction, at constant pressure, with the help of the following data:

Substance	Fe_2O_3(s)	Fe(s)	H_2(g)	H_2O(l)
C_p^0 (J mol^{-1} K^{-1})	104.5	25.5	28.9	75.3

Solution According to Kirchhoff's equation:

$$\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p\, dT$$

$$\begin{aligned}
\Delta C_p^0 &= 2C_p^0\ (\text{Fe}) + 3C_p^0\,(\text{H}_2\text{O}) - \left[\ C_p^0\,(\text{Fe}_2\text{O}_3) + 3C_p^0\,(\text{H}_2)\right]\\
&= 2\times25.5+3\times75.3-[104.5+3\times28.9]\\
&= 85.7 \text{ J K}^{-1}\text{ mol}^{-1}
\end{aligned}$$

Let the temperature at which ΔH is -28500 J be T

ΔH_2 or $\Delta H(T) = -28500$ J,

ΔH_1 or $\Delta H(298) = -35100$ J

$$-28500 = -35100 + \int_{298}^{T} (85.7)\,dT$$

or $\quad -28500 = -35100 + 85.7(T - 298)$

and $\quad T = 375 \text{ K} = 102°\text{C}$

5.2 HESS'S LAW

Hess's law states that the enthalpy change in a particular reaction is always constant and independent of the manner in which the reaction takes place.

According to this principle, the enthalpies of reactions can be added or subtracted algebraically.

For example,

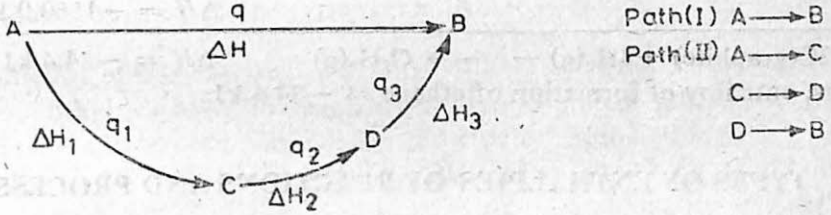

FIG. 5.1 *Diagram illustrating Hess's law*

According to Hess's law,

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

or

$$q = q_1 + q_2 + q_3$$

For example, carbon can be converted into CO_2 in two ways:

Path 1: $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5$ kJ

Path 2: $C(s) + \frac{1}{2}O_2 \longrightarrow CO(g) \qquad \Delta H_1 = -110.5$ kJ

$CO(g) + \frac{1}{2}O_2 \longrightarrow CO_2(g) \qquad \Delta H_2 = -283.0$ kJ

$C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5$ kJ

Thus, $\Delta H = \Delta H_1 + \Delta H_2$

EXAMPLE 5.5 (SI units) Calculate the enthalpy of allotropic transformation for

$C(\text{graphite}) \longrightarrow C(\text{diamond})$ from the following data:

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.51$ kJ (1)

$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -395.41$ kJ (2)

Solution The desired equation is

$C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H = ?$

This can be obtained by subtracting Eq. (2) from Eq. (1).

$C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.51$ kJ

$C(\text{diamond}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -395.41$ kJ

$C(\text{graphite}) \longrightarrow C(\text{diamond}) \qquad \Delta H = 1.90$ kJ

EXAMPLE 5.6 (SI units) Calculate the enthalpy of the reaction :

$$2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g)$$

from the following data:

(1) $C(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H = -393.5 \text{ kJ}$

(2) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ}$

(3) $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1560.0 \text{ kJ}$

Solution The required equation is

$$2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g)$$

Multiply Eq. (1) by 2 and Eq. (2) by 3 and add:

$2C(\text{graphite}) + 2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -787.0 \text{ kJ}$

$3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l) \qquad \Delta H = -857.4 \text{ kJ}$

(4) $2C(\text{graphite}) + 3H_2(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1644.4 \text{ kJ}$

Subtract Eq. (3) from the above Eq. (4)

$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \qquad \Delta H = -1560.0 \text{ kJ}$

$2C(\text{graphite}) + 3H_2(g) \longrightarrow C_2H_6(g) \qquad \Delta H = -84.4 \text{ kJ}$

Thus, enthalpy of formation of ethane = −84.4 kJ

5.3 TYPES OF ENTHALPIES OF REACTIONS AND PROCESSES

The various types of enthalpies* of reactions and processes are discussed below:

Enthalpy of Formation

The enthalpy change accompanying the formation of one mole of a compound from its elements is called the enthalpy of formation.

e.g. $C(\text{graphite}) + 2H_2(g) \longrightarrow CH_4(g) \qquad \Delta H = \Delta H_f$

$2C(s) + 3H_2 + 0.5O_2 \longrightarrow C_2H_5OH(l) \qquad \Delta H = \Delta H_f$

If all the species of the chemical reaction are in their standard states, the enthalpy of formation is called the standard enthalpy of formation, expressed as ΔH_f^o. The superscript 'o' indicates the *standard state*. The standard state of a substance is its most stable state under 1 atm (or 101.325 kPa) pressure.* The enthalpy of every element in its standard state is arbitrarily taken to be zero.

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*According to IUPAC (1981 recommendations), the different types of enthalpy changes are expressed by notations such as: the enthalpy of formation. $\Delta_f H$; the standard enthalpy of formation $\Delta_f H^\circ$; the enthalpy of combustion, $\Delta_c H$; the enthalpy change due to a reaction $\Delta_r H$, the enthalpy of dilution, $\Delta_{\text{dil}} H$, etc. In this notation, the symbol denoting the process is written as a subscript before the symbol for enthalpy. The changes in other properties are similarly expressed, e.g the change in molar standard entropy due to sublimation of a solid, $\Delta_{\text{sub}} S_m^o$; change in standard Gibbs free energy due to reaction, $\Delta_r G^\circ$. However, we use the older notations in the present book as the newer notation has not yet gained popularity.

It may be noted that the standard state is not restricted to 25°C, rather it can be expressed at any temperature. However, literature mostly records data at 25°C or 298.15 K.

The standard enthalpy change ΔH° for a reaction is equal to the difference of the sum of the enthalpies of formation of the products and the sum of the enthalpies of formation of the reactants in their standard states, i.e.

$$\Delta H^\circ = \Delta H^\circ_{f_{\text{products}}} - \Delta H^\circ_{f_{\text{reactants}}}$$

In earlier literature, the enthalpy change for various processes was also called the heat of process, e.g. heat of combustion, heat of solution, etc. IUPAC has discouraged the use of these terms and, therefore, we shall stick to the latest convention and talk about enthalpy of a given process. However, it may be remembered that enthalpy change is equal to heat absorbed by the system at constant pressure.

Enthalpy of Combustion

The enthalpy change accompanying the complete combustion of one mole of a substance is called the enthalpy of combustion.

$$CH_4(g)+2O_2(g) \longrightarrow CO_2(g)+2H_2O(l) \qquad \Delta H = \text{Enthalpy of combustion}$$

$$C_2H_5OH(g)+3O_2(g) \longrightarrow 2CO_2(g)+3H_2O(l) \quad \Delta H = \Delta H_c$$

Enthalpy of Neutralisation

The enthalpy change accompanying the neutralisation of one equivalent of an acid (or a base) by a base (or an acid) in sufficiently dilute aqueous solution is called the enthalpy of neutralisation of an acid (or a base).

e.g. $HCl(aq)+NaOH(aq) \longrightarrow NaCl(aq)+H_2O \quad \Delta H = \text{Enthalpy of neutralisation}$

or $H^+(aq)+OH^-(aq) \longrightarrow H_2O$

The enthalpy of neutralisation of all strong acids and bases is nearly constant and is -13.36 kcal (or -55.90 kJ mol^{-1}).

Enthalpy of Solution

The dissolution of a substance is accompanied by an enthalpy change called the enthalpy of solution.

The heat liberated in this case is $= -\Delta H_{\text{sln}}$. For example,

$$\text{Urea}(s)+nH_2O(l) \longrightarrow \text{Urea}(aq, m)\,;\ \Delta H = \Delta H_{\text{sln}}$$

The value of ΔH_{sln} depends on the final concentration of solute in the solution. It is also called the *integral enthalpy of solution*. If the solvent is in a large excess so that further dilution does not change

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*Recently, IUPAC has recommended that standard pressure should be taken as 1 bar (100 k Pa).

ΔH_{sln}, it is called the enthalpy of solution at infinite dilution. The *differential or partial enthalpy of solution* is an enthalpy change when one mole of solute is added to a sufficiently large quantity of solution so that the final concentration is not much different from the original.

Solution (c)+1 mole Solute = Solution (c) ΔH_{sln} (diff.)

At infinite dilution, the differential and integral enthalpies of solution become identical.

Enthalpy of Hydration

This is the enthalpy change accompanying the hydration of one mole of anhydrous salt to give the hydrated salt.

e.g. $CuSO_4(s)+5H_2O = CuSO_4 \cdot 5H_2O$ ΔH = Enthalpy of hydration $= \Delta H_{\text{hyd}}$

EXAMPLE 5.7 (SI units) Calculate the enthalpy of formation of liquid ethanol from the following data :

(a) $C_2H_5OH(l)+3O_2(g) \longrightarrow 2CO_2(g)+3H_2O(l)$ $\Delta H = -1367.8$ kJ

(b) $C(s)+O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(c) $H_2(g)+\frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H = -285.8$ kJ

Solution The enthalpy of formation of ethanol,

$$2C(s)+3H_2(g)+\tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H = ?$$

Multiply Eq. (b) by 2 and Eq. (c) by 3 and add

$$2C(s)+2O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -787.0 \text{ kJ}$$
$$3H_2(g)+\tfrac{3}{2}O_2(g) \longrightarrow 3H_2O(l) \qquad \Delta H = -857.4 \text{ kJ}$$

$$2C(s)+3H_2(g)+\tfrac{7}{2}O_2(g) \longrightarrow 2CO_2(g)+3H_2O(l) \qquad \Delta H = -1644.4 \text{ kJ}$$

Subtract Eq. (a)

$$C_2H_5OH(l)+3O_2(g) \longrightarrow 2CO_2(g)+3H_2O(l) \qquad \Delta H = -1367.8 \text{ kJ}$$

$$2C(s)+3H_2(g)+\tfrac{1}{2}O_2(g) \longrightarrow C_2H_5OH(l) \qquad \Delta H = -276.6 \text{ kJ}$$

Enthalpy of formation of ethanol = −276.6 kJ

EXAMPLE 5.8 (SI units) The enthalpies of combustion of carbon and carbon monoxide in excess of oxygen, at 298 K and constant pressure, are −393.5 kJ and −283.0 kJ respectively. Calculate the enthalpy and energy of formation of carbon monoxide.

Solution The enthalpy of formation of carbon monoxide is represented as

$$C(s)+\tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = ?$$

Given that (i) $C(s)+O_2(g) \longrightarrow CO_2(g)$ $\Delta H = -393.5$ kJ

(ii) $CO(g)+\frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\Delta H = -283.0$ kJ

Subtract Eq. (ii) from (i)

$$C(s)+\tfrac{1}{2}O_2(g) \longrightarrow CO(g) \qquad \Delta H = -110.5 \text{ kJ}$$

Thus, enthalpy of formation of CO(g) = −110.5 kJ

(ii) To calculate the energy of formation, i.e. ΔU we use

$$\Delta H = \Delta U + \Delta nRT$$

$\Delta H = -110.5$ kJ, $\Delta n = 1-\frac{1}{2} = \frac{1}{2}$, $T = 273+25 = 298$ K,

$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$\therefore \quad -110.5 \text{ kJ} = \Delta U + (\frac{1}{2} \text{ mol}) \times (8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})$

or $\quad \Delta U = -111.7 \text{ kJ}$

Energy of formation $= -111.7$ kJ

EXAMPLE 5.9 (SI units) Calculate the standard enthalpy of formation of naphthalene ($C_{10}H_8$) when the standard enthalpy of combustion of naphthalene is -5153 kJ and the standard enthalpies of formation of CO_2 and H_2O are -393.5 and -285.8 kJ respectively.

Solution The desired equation is

$10\ C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s) \qquad \Delta H^\circ = ?$

Given that

(a) $C_{10}H_8(s) + 12\ O_2(g) \longrightarrow 10\ CO_2(g) + 4H_2O(l) \qquad \Delta H^\circ = -5153 \text{ kJ}$

(b) $C(s) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\circ = -393.5 \text{ kJ}$

(c) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta H^\circ = -285.8 \text{ kJ}$

Multiply Eq. (b) by 10 and Eq. (c) by 4 and add

$10\ C(s) + 10\ O_2(g) \longrightarrow 10\ CO_2(g) \qquad \Delta H^\circ = -3935.0 \text{ kJ}$

$4H_2(g) + 2O_2(g) \longrightarrow 4H_2O(l) \qquad \Delta H^\circ = -1143.2 \text{ kJ}$

$10\ C(s) + 4H_2(g) + 12\ O_2(g) \longrightarrow 10\ CO_2(g) + 4H_2O(l) \qquad \Delta H^\circ = -5078.2 \text{ kJ}$

Subtract Eq. (a)

$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l) \quad \Delta H^\circ = -5153 \text{ kJ}$

$10\ C(s) + 4H_2(g) \longrightarrow C_{10}H_8(s) \qquad \Delta H^\circ = 74.8 \text{ kJ}$

Thus, enthalpy of formation of naphthalene $= 74.8$ kJ

EXAMPLE 5.10 (SI units) Calculate ΔH and ΔU for the following reaction

$4NH_3(g) + 5O_2(g) \longrightarrow 6H_2O(g) + 4NO(g)$

The standard enthalpies of formation of $NH_3(g)$, $H_2O(g)$ and $NO(g)$ are -46.19, -241.84 and 90.37 kJ, respectively.

Solution The given equation is

$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 6H_2O(g) + 4NO(g)$

$\Delta H =$ Enthalpies of products $-$ Enthalpies of reactants

$= 6 \times \Delta H_f^\circ (H_2O) + 4\ \Delta H_f^\circ (NO) - \left[4\Delta H_f^\circ (NH_3) + 5\Delta H_f^\circ (O_2) \right]$

$= 6 \times (-241.84) + 4 \times (90.37) - 4 \times (-46.19) - 0$

$= -904.8 \text{ kJ}$

Also $\Delta H = \Delta U + \Delta nRT$

$\Delta H = -904800 \text{ J}, \qquad n = 6 + 4 - (4 + 5) = 1,$

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, \qquad T = 298 \text{ K}$

$\Delta U = \Delta H - \Delta nRT$

$= -904800 - (1 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$

$= -907.28 \text{ kJ}$

EXAMPLE 5.11 The enthalpy of solution of anhydrous $CuSO_4$ and $CuSO_4 \cdot 5H_2O$ are -15.89 and 2.80 kcal respectively. Calculate the enthalpy of hydration of $CuSO_4$ to $CuSO_4 \cdot 5H_2O$.

Solution The desired equation is

$$CuSO_4(s) + 5H_2O(l) \longrightarrow CuSO_4 \cdot 5H_2O(s) \qquad \Delta H = ?$$

Given that,

$$CuSO_4(s) + aq \longrightarrow CuSO_4(aq) \qquad \Delta H_1 = -15.89 \text{ kcal}$$
$$CuSO_4 \cdot 5H_2O + aq \longrightarrow CuSO_4(aq) \qquad \Delta H_2 = 2.80 \text{ kcal}$$

The process may be expressed as

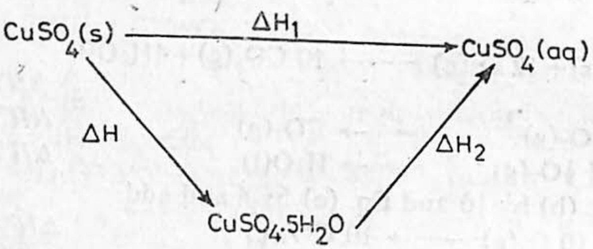


FIG. 5.2 *Calculation of enthalpy of hydration of $CuSO_4$ to $CuSo_4 \cdot 5H_2O$ using Hess's law.*

According to Hess's law,

$$\Delta H_1 = \Delta H + \Delta H_2$$

or $\Delta H = \Delta H_1 - \Delta H_2 = -15.89 - 2.80$

$$= -18.69 \text{ kcal}$$

Thus, heat of hydration of $CuSO_4 = -18.69$ kcal

5.4 BOND ENERGIES AND BOND ENTHALPIES

The amount of energy required to break a bond between two atoms in a molecule in the gaseous state is called the bond dissociation energy.

When a molecule contains more than one bond of the same type, the average value of the dissociation energies of a given bond is taken. The average value of the bond dissociation energies is called the bond energy, e.g. the bond dissociation energies of the C – H bond are :

$$CH_4\ (g) \longrightarrow CH_3\ (g) + H\ (g) \qquad \Delta H = 435 \text{ kJ mol}^{-1}$$
$$CH_3\ (g) \longrightarrow CH_2\ (g) + H\ (g) \qquad \Delta H = 370 \text{ kJ mol}^{-1}$$
$$CH_2\ (g) \longrightarrow CH\ (g) + H\ (g) \qquad \Delta H = 385 \text{ kJ mol}^{-1}$$
$$CH\ (g) \longrightarrow C\ (g) + H\ (g) \qquad \Delta H = 339 \text{ kJ mol}^{-1}$$

The bond energy is the average of these four values, i.e. 382 kJ mol^{-1}. The bond energy values can be used in estimating the enthalpy of formation ofcompounds and enthalpy of reactions.

EXAMPLE 5.12 (SI units) (a) Calculate ΔH° for the reaction

$$C_2H_4\ (g) + 3O_2\ (g) \longrightarrow 2CO_2\ (g) + 2H_2O\ (g)$$

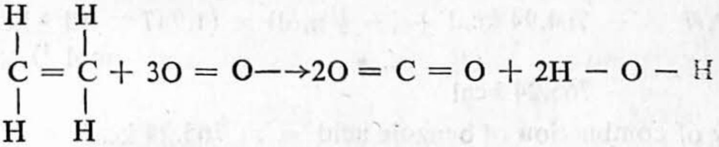
The average bond energies of various bonds are

Bond	C−H	O=O	C=O	O—H	C=C
Energy (kJ mol^{-1})	414	499	724	460	619

(b) Compare the value of ΔH° obtained by using the enthalpy of formation data : $\Delta H_f^\circ [CO_2 (g)] = -393.5$ kJ mol^{-1}, $\Delta H_f^\circ [H_2O (g)]$

$= -241.8$ kJ mol^{-1} and $\Delta H_f^\circ [C_2H_4 (g)] = 52.3$ kJ mol^{-1}.

Solution In this reaction, four C−H, one C=C and three O=O bonds are broken and four C=O and four O—H bonds are formed:



$$\begin{array}{c}H\quad H\\ |\quad\ |\\ C=C\\ |\quad\ |\\ H\quad H\end{array} + 3O=O \longrightarrow 2O=C=O + 2H-O-H$$

$$\therefore\ \Delta H^\circ = 4\Delta H(C-H) + \Delta H(C=C) + 3\Delta H(O=O) - 4\Delta H(C=O) - 4\Delta H(O-H)$$

$$= 4(414) + 619 + 3(499) - 4(724) - 4(460)$$

$$= -964 \text{ kJ mol}^{-1}$$

(b) Using enthalpy of combustion data

$$\Delta H^\circ = 2\Delta H_f^\circ\ (CO_2) + 2\Delta H_f^\circ\ (H_2O) - [\Delta H_f^\circ\ (C_2H_4) + 3\Delta H_f^\circ\ (O_2)]$$

$$= 2 \times (-393.5) + 2(-241.8) - [52.3 + 3 \times 0]$$

$$= -1322.9 \text{ kJ}$$

Thus, the enthalpy of reaction calculated from bond enthalpies is much lower than the actual value and therefore, the values so estimated are approximate.

MISCELLANEOUS EXAMPLES

EXAMPLE 5.13 In a bomb calorimeter 0.5 g of benzoic acid was subjected to combustion at 25°C. The temperature of the calorimeter system (including water) was found to rise by 0.55°C. Calculate the heat of combustion of benzoic acid at (i) constant volume (ii) constant pressure. The thermal capacity of the calorimeter system is 5.70 kcal K^{-1}.

Solution (i) Calculation of heat of combustion at constant volume

Weight of benzoic acid = 0.5 g
Rise in temperature = 0.55°C
Thermal capacity of calorimeter system = 5.70 kcal K^{-1}

Heat liberated when 0.5 g of benzoic acid undergoes combustion

$$= 0.55 \times 5.70 \text{ kcal}$$

$$\text{Heat liberated for one mole of benzoic acid} = \frac{0.55 \times 5.70 \times 122}{0.5}$$

$$= 764.94 \text{ kcal}$$

Energy of combustion of benzoic acid $= -\ 764.94$ kcal

(ii) Calculation of enthalpy of combustion (ΔH)

The combustion of benzoic acid may be represented as

$$C_6H_5COOH(s) + \frac{15}{2} O_2(g) \longrightarrow 7CO_2(g) + 3H_2O(l)$$

$$\Delta H = \Delta U + \Delta nRT$$

$$\Delta n = 7 - \frac{15}{2} = -\frac{1}{2}, \qquad R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1},$$

$$T = 273 + 25 = 298 \text{ K}$$

$$\Delta H = -\ 764.94 \text{ kcal} + (-\tfrac{1}{2} \text{ mol}) \times (1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$$

$$= -\ 765.24 \text{ kcal}$$

Enthalpy of combustion of benzoic acid $= -\ 765.24$ kcal

EXAMPLE 5.14 (SI units) Enthalpy of neutralisation of CH_3COOH by NaOH is -50.6 kJ mol^{-1}. Calculate ΔH for the ionization of CH_3COOH.

Solution The neutralisation of a strong acid with a strong base may be represented as

$$H^+(aq) + OH^-(aq) = H_2O(l) \qquad \Delta H = -\ 55.9 \text{ kJ mol}^{-1}$$

The neutralisation of acetic acid (CH_3COOH):

$$CH_3COOH(aq) = H^+(aq) + CH_3COO^- \qquad \Delta H_{\text{ionisation}}$$

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \qquad \Delta H = -\ 55.9 \text{ kJ mol}^{-1}$$

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l) \quad \Delta H_{\text{neutralisation}}$$

Obviously,

$$\Delta H_{\text{neutralisation}} = \Delta H_{\text{ionisation}} + (-55.9 \text{ kJ mol}^{-1})$$

or $$-50.6 \text{ kJ mol}^{-1} = \Delta H_{\text{ionisation}} - 55.9 \text{ kJ mol}^{-1}$$

$\therefore$ $$\Delta H_{\text{ionisation}} = -50.6 + 55.9 = 5.3 \text{ kJ mol}^{-1}$$

EXAMPLE 5.15 (SI units) The enthalpies of formation of some hydrocarbons are

Hydrocarbon	CH_4	C_2H_6	C_2H_4	C_2H_2	C_4H_{10}
ΔH_f° (kJ mol^{-1})	-74.8	-84.7	52.3	226.7	-126.1

Arrange them in the order of their efficiency, as fuel per gram (Enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -393.5 and -285.8 kJ mol^{-1}, respectively).

Solution The fuel efficiency can be calculated from the amount of heat evolved for every gram of fuel consumed. This can be done by first calculating the heat of combustion of these hydrocarbons:

(i) CH_4 The combustion of CH_4,

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H_{\text{combustion}} = \Delta H_f^\circ\ (CO_2) + 2\Delta H_f^\circ\ (H_2O) - \Delta H_f^\circ\ (CH_4) - 2\Delta H_f^\circ\ (O_2)$$

$$[\Delta H_f^\circ\ (O_2) = \text{zero}]$$

$$= -\ 393.5 + 2 \times (-285.8) - (-74.8)$$
$$= -\ 890.3 \text{ kJ mol}^{-1}$$

Mol. mass of $CH_4 = 16 \text{ g mol}^{-1}$

Heat evolved per gram $(q_p) = \dfrac{890.3 \text{ kJ mol}^{-1}}{16 \text{ g mol}^{-1}} = 55.64 \text{ kJ g}^{-1}$

(ii) C_2H_6 The combustion of C_2H_6,

$$C_2H_6(g) + 7/2\ O_2\ (g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H_{\text{combustion}} = 2\ \Delta H_f^\circ\ (CO_2) + 3\Delta H_f^\circ\ (H_2O) - \Delta H_f^\circ\ (C_2H_6)$$
$$= 2 \times (-393.5) + 3 \times (-285.8) - (-84.7)$$
$$= -\ 1559.7 \text{ kJ mol}^{-1}$$

Mol. mass of $C_2H_6 = 30 \text{ g mol}^{-1}$

Heat evolved per gram $(q_p) = \dfrac{1559.7 \text{ kJ mol}^{-1}}{30 \text{ g mol}^{-1}} = 51.99 \text{ kJ g}^{-1}$

(iii) C_2H_4 The combustion of C_2H_4,

$$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$$

$$\Delta H_{\text{combustion}} = 2\Delta H_f^\circ\ (CO_2) + 2\Delta H_f^\circ\ (H_2O) - \Delta H_f^\circ\ (C_2H_4)$$
$$= 2 \times (-393.5) + 2(-285.8) - (52.3)$$
$$= -\ 1410.9 \text{ kJ mol}^{-1}$$

Mol. mass of $C_2H_4 = 28 \text{ g mol}^{-1}$

Heat evolved per gram $= \dfrac{1410.9 \text{ kJ mol}^{-1}}{28 \text{ g mol}^{-1}} = 50.39 \text{ kJ g}^{-1}$

(iv) C_2H_2 The combustion of C_2H_2,

$$C_2H_2(g) + 5/2\ O_2(g) \longrightarrow 2\ CO_2(g) + H_2O(l)$$

$$\Delta H_{\text{combustion}} = 2\Delta H_f^\circ\ (CO_2) + \Delta H_f^\circ\ (H_2O) - \Delta H_f^\circ\ (C_2H_2)$$
$$= 2 \times (-393.5) + (-285.8) - (226.7)$$
$$= -\ 1299.5 \text{ kJ mol}^{-1}$$

Mol. mass of $C_2H_2 = 26 \text{ gm mol}^{-1}$

Heat evolved per gram $(q_p) = \dfrac{1299.5 \text{ kJ mol}^{-1}}{26 \text{ g mol}^{-1}} = 49.98 \text{ kJ g}^{-1}$

(v) C_4H_{10} The combustion of C_4H_{10},

$$C_4H_{10}(g) + 13/2\ O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$$

$$\Delta H_{\text{combustion}} = 4\ \Delta H_f^\circ\ (CO_2) + 5\Delta H_f^\circ\ (H_2O) - \Delta H_f^\circ\ (C_4H_{10})$$
$$= 4 \times (-393.5) + 5 \times (-285.8) - (-126.1)$$
$$= -\ 2876.9 \text{ kJ mol}^{-}1$$

Mol. mass of $C_4H_{10} = 58 \text{ g mol}^{-1}$

Heat evolved per gram $(q_p) = \dfrac{2876.9 \text{ kJ mol}^{-1}}{58 \text{ g mol}^{-1}} = 49.6 \text{ kJ g}^{-1}$

Thus, decreasing order of fuel efficiency :

$$CH_4 > C_2H_6 > C_2H_4 > C_2H_2 > C_4H_{10}$$

EXAMPLE 5.16 A person takes 15 breaths/min. The amount of air inhaled in each breath is about 450 ml and contains 21% oxygen by volume, while the exhaled air contains 16.1% oxygen by volume. If all the oxygen is used for converting sugar into $CO_2(g)$ and $H_2O(l)$, how much sucrose is burnt in the body in one day and what is the heat evolved (Enthalpy of combustion of sucrose is -5645 kJ mol^{-1}) ?

Solution Oxygen inhaled in each breath $= \dfrac{450 \times 21}{100}$ ml

Oxygen exhaled in each breath $= \dfrac{450 \times 16.1}{100}$ ml

Oxygen taken up in the body per breath $= \dfrac{450}{100}\left(21 - 16.1\right)$

$= \dfrac{450}{100} \times 4.9$ ml

Oxygen taken up in the body per day $= \dfrac{450}{100} \times 4.9 \times 15 \times 60 \times 24 = 476.28\ l$

Moles of O_2 taken in the body, $n = \dfrac{pV}{RT}$

$p = 1$ atm, $V = 476.28\ l$, $R = 0.082\ l$ atm mol^{-1} K^{-1}

$T = 25 + 273 = 298$ K (room temperature)

$$n = \frac{(1 \text{ atm}) \times (476.28\ l)}{(0.082\ l \text{ atm mol}^{-1} \text{ K}^{-1}) \times (298 \text{ K})} = 19.49 \text{ mol}$$

Sucrose can be burnt as:

$$C_{12}H_{22}O_{11}\ (s) + 12O_2\ (g) \longrightarrow 12CO_2\ (g) + 11H_2O\ (l)$$
$$\Delta H = -5645 \text{ kJ mol}^{-1}$$

Now, 12 mol of oxygen burns 1 mole or 342 g of sucrose

19.49 mol of oxygen will burn $= \dfrac{342 \times 19.49}{12}$

$= 555.5$ g of sucrose

1 mol or 342 g of sucrose, on combustion, liberates heat = 5645 kJ

555.5 g of sucrose will, on combustion, liberate heat $= \dfrac{5645 \times 555.5}{342}$

$= 9169$ kJ

QUESTIONS

Numerical Problems

5.1 (SI Units) The enthalpy of combustion of benzoic acid (C_6H_5COOH) at 25°C and 1 atm pressure is -2546.0 kJ mol^{-1}. What is ΔU for the reaction?

5.2 (SI Units) The standard molar enthalpy of N_2 at 298 K is zero. Calculate the value at 328 K ($C_{p,m}$ for $N_2 = 29.12$ J K^{-1} mol^{-1}).

5.3 (SI Units) The ΔH° for the reaction

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

at 27°C is -565.9 kJ mol^{-1} and C_p's are

$$C_{p,m}(CO) = 28.41 + 4.10 \times 10^{-3}\,T - 4.6 \times 10^{4}\,T^{-2}$$
$$C_{p,m}(O_2) = 29.96 + 4.18 \times 10^{-3}\,T - 1.67 \times 10^{5}\,T^{-2}$$
$$C_{p,m}(CO_2) = 44.22 + 8.79 \times 10^{-3}\,T - 8.62 \times 10^{5}\,T^{-2}$$

Calculate ΔH° for this reaction at 1000 K.

5.4 The enthalpy of vaporization of water

$$H_2O(l) \longrightarrow H_2O(g)$$

at 25°C is 44.0 kJ mol^{-1}. Calculate the enthalpy of vaporization at 100°C. $C_{p,m}[H_2O(l)] = 75.30$ J K^{-1} mol^{-1}, $C_{p,m}[H_2O(g)] = 33.6$ J K^{-1} mol^{-1}.

5.5 The enthalpy of formation of steam from gaseous hydrogen and oxygen is -241.8 kJ mol^{-1} at 25°C. The constant-pressure molar heat capacities of hydrogen, oxygen and water are 28.8, 29.4 and 33.6 J K^{-1} mol^{-1} respectively. Calculate the enthalpy of steam at 125°C.

5.6 (SI Units) The enthalpies of formation of $H_2O(l)$, $CO_2(g)$ and $C_3H_8(g)$ are -285, -393 and -104 kJ mol^{-1} respectively. Calculate the enthalpy of combustion of propane.

5.7 What is the enthalpy of phase transition

$$S(\text{rhombic}) \longrightarrow S(\text{monoclinic})$$

If $S(\text{rhombic}) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H^\circ = -296.06$ kJ

$S(\text{monoclinic}) + O_2(g) \longrightarrow SO_2(g) \qquad \Delta H^\circ = -296.36$ kJ

5.8 Enthalpies of formation of FeO(s) and Fe_2O_3(s) are -267.9 and -822.2 kJ, respectively. Calculate the enthalpy of the reaction

$$2\,FeO(s) + \tfrac{1}{2}\,O_2(g) \longrightarrow Fe_2O_3(s)$$

5.9 (SI Units) The molar enthalpies of fusion and vaporization of water are 6.0 kJ mol^{-1} and 44.0 kJ mol^{-1}, respectively. Calculate the molar enthalpy of sublimation of ice.

5.10 (SI Units) From the following neutralization data of a weak acid (HA),

$$HA + OH^- \longrightarrow A^- + H_2O \qquad \Delta H = -41.80 \text{ kJ}$$
$$H^+ + OH^- \longrightarrow H_2O \qquad \Delta H = -55.90 \text{ kJ}$$

Calculate the enthalpy of dissociation of HA.

5.11 The enthalpy of neutralization and enthalpy of ionization of HCN are -12.13 and 43.77 kJ mol^{-1}, respectively. Calculate the enthalpy of neutralization of a strong acid with a strong base.

5.12 (SI Units) The enthalpies of neutralization for CH_3COOH with NaOH and NH_4OH with HCl are -50.6 and -51.4 kJ mol^{-1}, respectively. Calculate the enthalpy of neutralization of CH_3COOH and NH_4OH.

5.13 (SI Units) The enthalpy of formation of gaseous hydrogen peroxide is -130.0 kJ mol^{-1} and enthalpies of H(g) and O(g) are $+217.5$ and $+248$ kJ mol^{-1}. Calculate the bond enthalpy of the O$-$O bond if that for the O$-$H bond is 462 kJ mol^{-1}.

5.14 (SI Units) Acetaldehyde reacts with hydrogen gas to form ethyl alcohol. Calculate the enthalpy of the reaction from the following bond enthalpies data:

H—H $= 436$ kJ mol^{-1} O—H $= 463$ kJ mol^{-1}
C—O $= 351$ kJ mol^{-1} C—H $= 413$ kJ mol^{-1}
C=O $= 732$ kJ mol^{-1}

5.15 (SI Units) Calculate the enthalpy of formation of KOH(s) from the following data :

$K(s) + H_2O(1) + aq \longrightarrow KOH(aq) + \frac{1}{2} H_2(g)$ $\Delta H = -195$ kJ
$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(1)$ $\Delta H = -285$ kJ
$KOH(s) + aq \longrightarrow KOH(aq)$ $\Delta H = -55$ kJ

5.16 The heat of solution of $BaCl_2 \cdot 2H_2O$ is 2.1 kcal and the heat of hydration of anhydrous $BaCl_2$ is -7.03 kcal. What is the heat of solution of anhydrous $BaCl_2$?

5.17 (SI Units) On dissolving 100 g of anhydrous $CuSO_4$ in water, the heat evolved is 41.7 kJ. The same amount of the crystalline substance $CuSO_4 \cdot 5H_2O$, on dissolving, absorbed 4.7 kJ. Calculate the heat of hydration of $CuSO_4$ per mole.

5.18 Calculate the enthalpy of formation of anhydrous Al_2Cl_6 from the following data:

$2Al(s) + 6HCl(aq) \longrightarrow Al_2Cl_6(aq) + 3H_2(g)$ $\Delta H = -240$ kcal
$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $\Delta H = -44$ kcal
$HCl(g) + (aq) \longrightarrow HCl(aq)$ $\Delta H = -105$ kcal
$Al_2Cl_6(s) + aq \longrightarrow Al_2Cl_6(aq)$ $\Delta H = -153.7$ kcal

5.19 At constant volume and 27°C,

$2C_6H_6(1) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(1) + 1600$ kcal
$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(1) + 620$ kcal

Calculate the enthalpy of conversion of acetylene into 1 mol of benzene, at constant pressure and 27°C.

5.20 (SI Units) Calculate ΔH for the reaction

$K(s) + \frac{1}{2} F_2(g) \longrightarrow KF(s)$

from the following data

$K(s) \longrightarrow K(g)$ $\Delta H = 90.0$ kJ
$K(g) \longrightarrow K^+(g) + e^-$ $\Delta H = 418.8$ kg
$F_2(g) \longrightarrow 2F(g)$ $\Delta H = 150.6$ kJ
$F^-(g) \longrightarrow F(g) + e^-$ $\Delta H = 333.0$ kJ
$KF(s) \longrightarrow K^+(g) + F^-(g)$ $\Delta H = 803.3$ kJ

5.21 (SI Units) The enthalpies of formation of ethane, propane, butane, $CO_2(g)$ and $H_2O(1)$ are -84.6, -107.6, -126.1, -393.5 and -285.8 kJ mol^{-1}, respectively. Which of ethane, propane and butane can be used as an efficient fuel on mass basis.

5.22 (SI Units) The enthalpy of atomization of hydrazine, according to the equation

$$N_2H_4(g) \longrightarrow 2N(g) + 4H(g)$$

is $\Delta H^\circ_{\text{at}} = 1724$ kJ mol^{-1}. Estimate ΔH° for fission of the N—N bond if ΔH° for fission of the N—H bond is 391 kJ mol^{-1}.

5.23 (SI Unit) How much heat will be produced in slaking 5 kg of quicklime (CaO) according to the reaction,

$$CaO(s) + H_2O(1) \longrightarrow Ca(OH)_2(s)$$

$\Delta H_f^\circ \left[CaO(s) \right] = -634$ kJ mol^{-1}
$\Delta H_f^\circ \left[H_2O(1) \right] = -286$ kJ mol^{-1}
$\Delta H_f^\circ \left[Ca(OH)_2(s) \right] = -986$ kJ mol^{-1}

5.24 How much heat is required to convert 1 kg of ice at $-10°C$ to steam at $110°C$? (Assume specific heat of ice, water and steam are 0.5, 1.0 and 0.5 cal g^{-1} K^{-1}).

5.25 (SI Units) Estimate the enthalpy of combustion of 5 dm^3 n-octane (density $=0.7$ kg dm^{-3}) in excess oxygen giving $CO_2(g)$ and $H_2O(g)$ from the following bond enthalpies data :

Bond	C−C	C−H	O−H	C=O	O=O
Bond enthalpy (kJ mol^{-1})	348	413	463	732	498

QUIZ QUESTIONS

Type A: Multiple Choice

5.26 The variation of enthalpy of reaction with temperature is given by
(a) Arrhenius equation
(b) Kirchhoff's equation
(c) Hess's law
(d) Claussius Clapeyron equation

5.27 ΔH and ΔU for the reaction $S(s) + 3/2\,O_2(g) \longrightarrow SO_3(g)$ are related as
(a) $\Delta H = \Delta U + RT$
(b) $\Delta H = \Delta U - 0.5\,RT$
(c) $\Delta H = \Delta U + 3/2\,RT$
(d) $\Delta H = \Delta U - 3/2\,RT$

5.28 In which of the following neutralization reactions will the enthalpy of neutralization be the smallest ?
(a) NaOH with HCl
(b) NaOH with CH_3COOH
(c) HCl with NH_4OH
(d) CH_3COOH with NH_4OH

5.29 In which of the following reactions is ΔH not equal to ΔU ?
(a) $HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O$
(b) $C(s) + O_2(g) \longrightarrow CO_2(g)$
(c) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$
(d) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

5.30 The enthalpy change accompanying the reaction

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) \text{ is}$$

(a) enthalpy of solution
(b) enthalpy of neutralization
(c) enthalpy of dilution
(d) enthalpy of precipitation

5.31 Which of the following enthalpies is always negative ?
(a) enthalpy of formation
(b) enthalpy of solution
(c) enthalpy of combustion
(d) enthalpy of melting

5.32 The enthalpies of combustions are
$\Delta H_c\,(C_2H_6) = -1560$ kJ
$\Delta H_c\,(C_2H_4) = -1411$ kJ
$\Delta H_c\,(C_4H_{10}) = -2877$ kJ
$\Delta H_c\,(CH_4) = -890.4$ kJ

Which of these has the lowest efficiency as fuel, per gram?

(a) C_2H_6 (b) C_2H_4

(c) C_4H_{10} (d) CH_4

5.33 For which of the following reactions is ΔH less than ΔU?

(a) $C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6CO_2(g) + 6H_2O(l)$

(b) $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$

(c) $N_2O_4(g) \longrightarrow 2NO_2(g)$

(d) $N_2(g) + O_2(g) \longrightarrow 2NO(g)$

5.34 For the reaction

$C(s) + \frac{1}{2} O_2(g) \longrightarrow CO(g)$,

which is correct ?

(a) $\Delta H < \Delta U$

(b) $\Delta H = \Delta U$

(c) $\Delta H > \Delta U$

(d) none of these

5.35 According to Kirchhoff's equation, the enthalpies at two temperatures are

(a) $\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_V \, dT$

(b) $\Delta H_2 - \Delta H_1 = \int_{T_2}^{T_1} \Delta C_p \, dT$

(c) $\Delta H_1 = \Delta H_2 + \int_{T_1}^{T_2} \Delta C_p \, dT$

(d) $\Delta H_2 = \Delta H_1 + \int_{T_1}^{T_2} \Delta C_p \, dT$

Type B: Multiple Choice (Numerical Problems)

5.36 The enthalpies of combustion of carbon and carbon monoxide are −393.5 kJ and −283 kJ, respectively. The enthalpy of formation of carbon monoxide is

(a) 110.5 kJ (b) 676.5 kJ

(c) −110.5 kJ (d) −676.5 kJ

5.37 The enthalpies of formation of gaseous N_2O and NO at 298 K are 82 and 90 kJ mol⁻¹. The enthalpy of the reaction $N_2O(g) + \frac{1}{2} O_2 \longrightarrow 2NO(g)$ is

(a) −8 kJ (b) 98 kJ

(c) −74 kJ (d) 8 kJ

5.38 The enthalpy of dissolution of $BaCl_2$ (s) and $BaCl_2 \cdot 2H_2O$ (s) are −20.6 and 8.8 kJ mol⁻¹ respectively. The enthalpy change for the reaction $BaCl_2$ (s) $+ 2H_2O \longrightarrow BaCl_2 \cdot 2H_2O$ (s) is

(a) 29.4 kJ (b) −29.4 kJ

(c) −11.8 kJ (d) 38.2 kJ

5.39 Consider the reaction:

$$SO_2(g) + \frac{1}{2} O_2(g) \longrightarrow SO_3(g) \qquad \Delta H = -98.3 \text{ kJ}$$

If the enthalpy of formation of $SO_3(g)$ is -395.4 kJ, then the enthalpy of formation of $SO_2(g)$ is

(a) 297.1 kJ	(b) 493.7 kJ
(c) -493.7 kJ	(d) -297.1 kJ

5.40 For the reaction $C_6H_6(l) + 7\frac{1}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$ $\Delta H(27°C) = -780.9$ kcal. ΔU for the reaction will be (assume $R \approx 2$ cal mol^{-1} K^{-1})

(a) -781.8 kcal	(b) -780.0 kcal
(c) -780.75 kcal	(d) -781.05 kcal

5.41 The enthalpies of combustion of C (graphite) and C (diamond) are -393.5 and -395.4 kJ mol^{-1} respectively. Enthalpy of conversion of C (graphite) to C (diamond) is

(a) 1.9 kJ	(b) -1.9 kJ
(c) -788.9 kJ	(d) 788.9 kJ

5.42 The enthalpy of a reaction at 273 K is -3.75 kJ. What will be the enthalpy of reaction at 373 K if $\Delta C_p =$ zero.

(a) -3.75 kJ

(b) zero

(c) $-3.75 \times \dfrac{373}{273}$ kJ

(d) -375 kJ

5.43 The enthalpy changes at 298 K in successive breaking of O–H bonds of water, are

$$H_2O(g) \longrightarrow H(g) + OH(g) \qquad \Delta H = 498 \text{ kJ mol}^{-1}$$
$$OH(g) \longrightarrow H(g) + O(g) \qquad \Delta H = 428 \text{ kJ mol}^{-1}$$

the bond enthalpy of the O–H bond is

(a) 498 kJ mol^{-1}	(b) 463 kJ mol^{-1}
(c) 428 kJ mol^{-1}	(d) 70 kJ mol^{-1}

5.44 For the reaction at 298 K,

$$H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(g) \qquad \Delta H = -242 \text{ kJ}$$

ΔC_p is -10 J K^{-1}. Calculate ΔH at 398 K.

(a) -1242 kJ	(b) -243 kJ
(c) -241 kJ	(d) -1.242 kJ

5.45 The enthalpy of neutralization of HCl by NaOH is -55.9 kJ and that of HCN by NaOH is -12.1 kJ mol^{-1}. The enthalpy of ionization of HCN is

(a) -68.0 kJ	(b) -43.8 kJ
(c) 68.0 kJ	(d) 43.8 kJ

Type C: True or False

5.46 Bond enthalpies of diatomic molecules is equal to bond enthalpies of dissociation.

5.47 If ΔC_p of a reaction is zero, enthalpy of reaction does not change with temperature.

5.48 At infinite dilution, differential and integral enthalpies of solution are equal.

5.49 Enthalpy of combustion is always negative.

5.50 ΔH is always greater than ΔU for reactions.

5.51 $\Delta H°$ for the combustion of $C_3H_6(g)$ to give $CO_2(g)$ and $H_2O(l)$ is less than $\Delta U°$.

5.52 The enthalpy of every element in its standard state, at all temperatures, is zero.

5.53 The enthalpy change in dissociating a molecule into its constituent atoms is called enthalpy of ionization.

5.54 The most common substance for the standardization of calorimeter is benzoic acid.

5.55 The enthalpy of neutralization of HCl by NaOH is less than the enthalpy of neutralization of CH_3COOH by NaOH.

ANSWERS

Numerical Problems

5.1 -2544.8 kJ mol^{-1} *5.2* 0.8736 kJ *5.3* -565.75 kJ *5.4* 40.872 kJ *5.5* -242.71 kJ *5.6* -2215 kJ mol^{-1} *5.7* 0.30 kJ *5.8* -286.4 kJ *5.9* 50.0 kJ *5.10* 14.10 kJ *5.11* -55.90 kJ *5.12* -46.1 kJ *5.13* 137 kJ mol^{-1} *5.14* -59 kJ mol^{-1} *5.15* -425 kJ *5.16* -4.93 kcal *5.17* -78.2 kJ *5.18* -323.3 kcal *5.19* -131.8 kcal *5.20* 552.2 kJ *5.21* C_2H_6 *5.22* 160 kJ mol^{-1} *5.23* 5892.8 kJ *5.24* The total ΔH can be calculated from the steps; ΔH_1 (heating ice from -10°C to ice at 0°C) $= 5$ kcal; ΔH_2 (melting of ice at 0°C) $= 80$ kcal; ΔH_3 (heating water from 0° to 100°C) $= 100$ kcal; ΔH_4 (vaporization to steam at 100°C) $= 540$ kcal; ΔH_5 (heating steam from 100° to 110°C) $= 5$ kcal. Thus $\Delta H = 730$ kcal *5.25* Calculate ΔH_c from the equation $C_8H_{18} + 12.5\ O_2 \longrightarrow 8CO_2 + 9H_2O\ \Delta H_c =$ $[16\Delta H(C{=}O) + 18\Delta H\,(O{-}H)] - [7\Delta H(C{-}C) + 18\Delta H\,(C{-}H) + 12.5\Delta H\,(O{=}O)]$ $= -3951$ kJ mol^{-1}, Moles of Octane $= 5.0\ dm^3 \times 700\ g\ dm^{-3}/114\ g\ mol^{-1}$ Enthalpy of combustion for 5.0 $dm^3 = 121.303 \times 10^3$ kJ mol^{-1}

Quiz Questions

5.26 (b) *5.27* (b) *5.28* (a) *5.29* (d) *5.30* (c) *5.31* (c) *5.32* (c) *5.33* (b) *5.34* (c) *5.35* (d) *5.36* (c) *5.37* (b) *5.38* (b) *5.39* (d) *5.40* (b) *5.41* (a) *5.42* (a) *5.43* (b) *5.44* (b) *5.45* (d) *5.46* True *5.47* True *5.48* True *5.49* True *5.50* False *5.51* True *5.52* False *5.53* False; It is called enthalpy of atomization *5.54* True *5.55* False

6

The Second and Third Laws of Thermodynamics

The first law of thermodynamics is concerned with the conservation of energy. However, it cannot determine the feasibility or spontaneity of a process which is decided by the second law of thermodynamics. The second law of thermodynamics helps us to predict whether a given process or chemical reaction can occur spontaneously or not and also helps to assess how far the reaction will proceed or the stage at which equilibrium will be established.

6.1 CYCLIC PROCESS AND CARNOT CYCLE

As defined in Ch. 4, a cyclic process is one in which the system, after undergoing various processes, returns to its initial state.

Since the internal energy of the system depends only upon its state, ΔU will be zero and the work done by the system during all these processes (steps of cyclic process) should be equal to the heat absorbed by it i.e.,

$$\Delta U = 0 = q + w \quad \text{or } q = -w$$

$$\text{or} \quad q_1 + q_2 + q_3 + \ldots = -[w_1 + w_2 + w_3 + \ldots]$$

where $q_1, q_2, q_3, \ldots$ are heats absorbed and $w_1, w_2, w_3, \ldots$ are works done in the several processes constituting the cycle.

A reversible cyclic process, when applied to an ideal gas, is called a *Carnot cycle*. The system may be taken as one mole of an ideal gas enclosed in a vessel fitted with a frictionless piston. The initial state of the system is represented by p_1, V_1 and T_1. The Carnot cycle is completed in the following four steps:

Step 1 The gas is expanded *isothermally* and *reversibly* so that pressure and volume change to p_2 and V_2, while temperature remains T_1.

$$\Delta U_1 = 0, \quad w_1 = -RT_1 \ln \frac{V_2}{V_1}$$

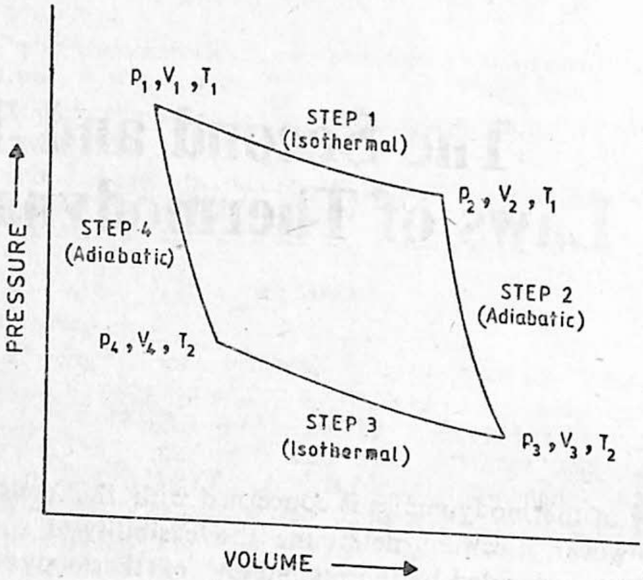


FIG. 6.1 *Carnot cycle consists of 4 processes. Steps 1 and 3 are isothermal whereas 2 and 4 are adiabatic.*

and $$q_1 = RT_1 \ln \frac{V_2}{V_1} \qquad (V_2 > V_1)$$

Step 2 The gas is expanded *adiabatically* and *reversibly*, from volume V_2 to V_3 and pressure p_2 to p_3. The temperature falls from T_1 to T_2. During this process,

$$\Delta U_2 = C_V (T_2 - T_1)$$

No heat is transferred in this process. Therefore, according to first law of thermodynamics,

$$q = 0$$

and $$w_2 = C_V (T_2 - T_1) \qquad (T_2 < T_1)$$

Step 3 The gas is compressed *reversibly* and *isothermally* to the state represented by p_4, V_4 and T_2. During this process,

$$\Delta U_3 = 0, \qquad w_3 = -RT_2 \ln \frac{V_4}{V_3}$$

and $$q_2 = RT_2 \ln \frac{V_4}{V_3} \qquad (V_4 < V_3).$$

Step 4 The gas is compressed *adiabatically* and *reversibly* so that it achieves the initial state (p_1, V_1, T_1). During this process,

$$\Delta U_4 = C_V (T_1 - T_2), \qquad q = 0$$

and $$w_4 = C_V (T_1 - T_2)$$

The overall energy change, work done on the gas and heat absorbed are

$$\Delta U = \Sigma \Delta U_i = 0 + C_V (T_2 - T_1) + 0 + C_V (T_1 - T_2) = 0$$

$$w = \Sigma w_i = -RT_1 \ln \frac{V_2}{V_1} + C_V (T_2 - T_1)$$

$$- RT_2 \ln \frac{V_4}{V_3} + C_V (T_1 - T_2)$$

$$= - RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_4}{V_3}$$

Steps 2 and 4 are adiabatic and therefore,

$$T_1^{C_V/R} \; V_2 = T_2^{C_V/R} V_3$$

and $$T_2^{C_V/R} \; V_4 = T_1^{C_V/R} \; V_1$$

$$\therefore \quad \frac{V_2}{V_3} = \frac{V_1}{V_4}$$

or $$\frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$\therefore \quad w = - R (T_1 - T_2) \ln \frac{V_2}{V_1}$$

Similarly,

$$q = \Sigma q_i = RT_1 \ln \frac{V_2}{V_1} + RT_2 \ln \frac{V_4}{V_3}$$

$$= R (T_1 - T_2) \ln \frac{V_2}{V_1}$$

It is obvious that for this cycle $q = -w$, i.e. work done by the gas is equal to the net heat absorbed.

6.2 EFFICIENCY OF THE TRANSFORMATION OF HEAT INTO WORK

It may be noted that the heat q_1 absorbed in a Carnot cycle, from the source at a higher temperature, is not completely converted into work. Some of it is uselessly rejected to the sink at lower temperature. The ratio of the network done during the cycle and the total heat absorbed $\left(\frac{-w}{q}\right)$ is called the *efficiency*, η, of the Carnot engine.

$$\text{Efficiency,} \quad \eta = \frac{-w}{q_1} = \frac{R (T_1 - T_2) \ln \dfrac{V_2}{V_1}}{RT_1 \ln \dfrac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1}$$

According to the first law of thermodynamics,

$-w = q_1 + q_2$ so that

$$\eta = \frac{T_1 - T_2}{T_1} = \frac{q_1 + q_2}{q_1}$$

Since $T_2 < T_1$, $\quad \eta < 1$

Also $q_1 + q_2 < q_1$ because q_2 is negative.

This shows that efficiency is always less than one, i.e. all the heat absorbed at a higher temperature is not converted into work. It is clear that the efficiency of a cyclic engine depends only on the temperatures T_1 and T_2 (i.e. of the source and the sink) and is independent of the nature of the engine fluid or the mode of operation of the engine. The *Carnot theorem* is expressed as—all cyclic engines working between the same temperatures of the source and the sink have the same efficiency.

Example 6.1 A heat engine works between 127°C and 27°C. Calculate the efficiency of the engine.

Solution Efficiency of an engine

$$\eta = \frac{T_1 - T_2}{T_1}$$

$$T_1 = 273 + 127 = 400\text{ K}, \qquad T_2 = 273 + 27 = 300\text{ K}$$

$$\therefore \qquad \eta = \frac{400 - 300}{400} = 0.25$$

Efficiency of the engine $= 25\%$

Example 6.2 Calculate the minimum amount of heat that must be withdrawn from the hot reservoir at 137°C to obtain work equivalent to 15 kJ per cycle. The temperature of the sink is 17°C.

Solution Efficiency of an engine is

$$\eta = \frac{T_1 - T_2}{T_1} \quad \text{and } \eta = \frac{-w}{q_1}$$

$$T_1 = 273 + 137 = 410\text{ K}, \qquad T_2 = 273 + 17 = 290\text{ K}, \qquad -w = 15\text{ kJ}$$

$$\eta = \frac{410 \quad 290}{410} = \frac{120}{410} = 0.29$$

Heat that must be withdrawn from the hot reservoir,

$$q_1 = \frac{-w}{\eta} = \frac{15}{0.29} = 51.72\text{ kJ}$$

6.3 CARNOT CYCLE AND ENTROPY

According to the Carnot cycle, efficiency is,

$$\frac{q_1 + q_2}{q_1} = \frac{T_1 - T_2}{T_1}$$

or

$$\frac{q_2}{T_2} + \frac{q_1}{T_1} = 0$$

A reversible cycle, can be considered to be consisting of a number of Carnot cycles (Fig. 6.2),

$$\Sigma \frac{q}{T} = 0$$

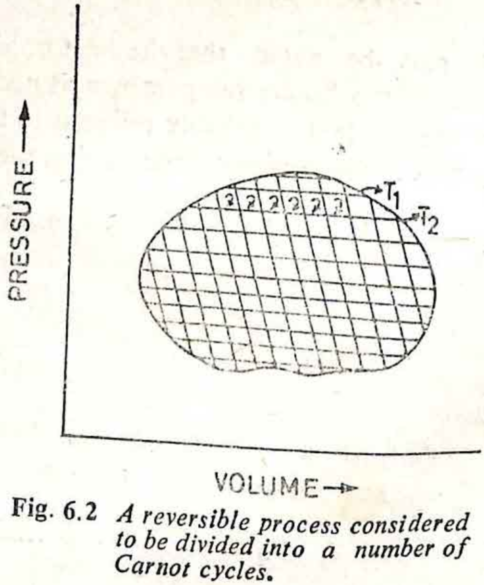


Fig. 6.2 *A reversible process considered to be divided into a number of Carnot cycles.*

When the changes are infinitesimal,

$$\Sigma \frac{dq}{T} = 0$$

In the limit, we replace summation by integration,

$$\int \frac{dq_{\text{rev}}}{T} = 0$$

This means that although the sum Σdq_i or $\int dq_{\text{rev}}$ for the process is not zero, but if it is divided by T it becomes equal to zero. This implies that dq_{rev}/T represents change in some thermodynamic property. This property is called *entropy* (S) and the change $\frac{dq_{\text{rev}}}{T}$, which represents entropy change, is dS. Thus,

$$dS = \frac{dq_{\text{rev}}}{T}$$

and

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

The units of entropy are cal K^{-1} which are expressed as eu. In the SI system, the units of entropy are J K^{-1} and these are represented by EU (1 eu = 4.184 EU).

6.4 STATEMENTS OF SECOND LAW OF THERMODYNAMICS

The second law of thermodynamics states that the entropy of an isolated system tends to increase and reaches a maximum value. This means that the most stable state of an isolated system is the state of maximum entropy. Since the universe may be considered an isolated system, it might be said that "the entropy of the universe is always increasing".

There are several other equivalent statements of the second law:

1. *Clausius* postulated that it is impossible to transfer heat from a cold to a hot reservoir without doing some work.

2. *Kelvin* postulated that it is impossible to take heat from a source and convert all of it into work, by a cyclic process, without losing some of it to a colder reservoir.

3. *Caratheodory* postulated that in the neighbourhood of every equilibrium state of a closed system, there are states which cannot be reached from the first state along any adiabatic path.

If any of the statements of the second law of thermodynamics is assumed to be true, then all others can be shown to be true. For example, if a system goes from state A to state B, either reversibly or irreversibly, then the entropy change is given by

$$\Delta S = \frac{q_{\text{rev}}}{T}$$

and the corresponding change in surroundings is $\Delta S = \frac{-q_{\text{rev}}}{T}$.

Then the total change of entropy of the system and the surroundings is

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{rev}}}{T} = 0$$

But if the system changes irreversibly and absorbs heat q_{irr}, then the corresponding change in surroundings is $\Delta S_{\text{surr}} = -q_{\text{irr}}/T$, so that

$$\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{\text{rev}}}{T} - \frac{q_{\text{irr}}}{T} > 0 \qquad \left(\because \; q_{\text{rev}} > q_{\text{irr}}\right)$$

Thus, in an irreversible process, the entropy of the system and the surroundings tends to increase.

6.5 ENTROPY CHANGES IN SOME PROCESSES

In general, the entropy change of a system is defined by the entropy of the final state minus the entropy of the initial state: $\Delta S = S_{\text{final}} - S_{\text{initial}}$.

Entropy Changes for an Ideal Gas

In going from state 1 to state 2, the entropy change (ΔS) is given by the following relations:

(a) When T and V are two variables

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_{V,m}}{T}\, dT + nR \ln \frac{V_2}{V_1}$$

If $C_{V,m}$ is independent of temperature,

$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

(b) When T and p are two variables

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_{p,m}}{T}\, dT - nR \ln \frac{p_2}{p_1}$$

or $$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1} \qquad \left(C_{p,m} \text{ is constant}\right)$$

For an *isothermal process* (T constant)

$$\Delta S = nR \ln \frac{V_2}{V_1} = -nR \ln \frac{p_2}{p_1}$$

For an *isobaric process* (p constant)

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_{p,m}}{T}\, dT,$$

Assuming $C_{p,m}$ independent of T,

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$$

For an isochoric process (V constant)

$$\Delta S = \int_{T_1}^{T_2} \frac{nC_{V,m}}{T} \, dT$$

Assuming $C_{V,m}$ independent of T,

$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1}$$

Entropy Change During Adiabatic Expansion

In such processes, $q = 0$ at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called *isoentropic processes.*

Entropy Change During Phase Transition

The change of matter from one state (solid, liquid or gas) into another is called phase transition. Such changes occur at definite temperatures (melting point, boiling point, etc.) and are accompanied by absorption or evolution of heat.

The entropy change,

$$\Delta S = \frac{q_{\text{trans}}}{T} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}$$

e.g.

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$\Delta S_{\text{evap}} = \frac{\Delta H_{\text{evap}}}{T_{\text{evap}}}$$

Example 6.3 **(SI units) Calculate the entropy change when 2 mol of an ideal gas expand isothermally and reversibly, from an initial volume of 1 dm^3 to a final volume of 10 dm^3 at 300 K.**

Solution For an isothermal process,

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

$n = 2.0$ mol, $R = 8.314$ J mol^{-1} K^{-1}, $V_1 = 1$ dm^3, $V_2 = 10$ dm^3

$$\therefore \quad \Delta S = (2.0 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times 2.303 \log 10/1$$
$$= 38.29 \text{ J K}^{-1}$$

Example 6.4 Helium, weighing 4 g, is expanded from 1 atm to one-tenth of the original pressure at 30°C. Calculate the change in its entropy, assuming it to be an ideal gas.

Solution The process is an isothermal expansion of gas. Therefore,

$$\Delta S = nR \ln \frac{p_1}{p_2}$$

$n = \frac{4}{4} = 1$ mol, $\quad R = 8.314$ J mol^{-1} K^{-1}, $\quad p_1 = 1$ atm,

$p_2 = 1/10$ atm

$$\therefore \quad \Delta S = (1 \text{ mol}) \times (8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times 2.303 \log \frac{1}{1/10}$$

$$= 19.15 \text{ J K}^{-1}$$

EXAMPLE 6.5 Fifty-four grams of water are heated from 17°C to 27°C, at constant pressure. Calculate the increase in entropy for this process. The molar heat capacity at constant pressure for water is 75.3 J K^{-1} mol^{-1}.

Solution The increase in entropy at constant pressure,

$$\Delta S = nC_{p,m} \ln \frac{T_2}{T_1}$$

$n = \frac{54}{18} = 3$ mol, $\quad C_{p,m} = 75.3$ J K^{-1} mol^{-1}, $\quad T_1 = 290$ K,

$T_2 = 300$ K

$$\therefore \quad \Delta S = (3 \text{ mol}) \times (75.3 \text{ J mol}^{-1} \text{ K}^{-1}) \times 2.303 \log \frac{300}{290}$$

$$= 7.66 \text{ J K}^{-1}$$

EXAMPLE 6.6 Two moles of an ideal gas ($C_{V,m} = 12.5$ J K^{-1} mol^{-1}) are at 300 K and occupy 2 dm^3. If the gas is heated to 325 K and the volume changed to 4 dm^3, calculate the entropy change.

Solution The entropy change, as a function of T and V, is

$$\Delta S = nC_{V,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$n = 2$ mol, $\quad C_{V,m} = 12.5$ J K^{-1} mol^{-1}, $\quad T_2 = 325$ K,

$T_1 = 300$ K, $\quad R = 8.314$ J K^{-1} mol^{-1}

$V_1 = 2$ dm^3, $\quad V_2 = 4$ dm^3.

$$\therefore \quad \Delta S = (2 \text{ mol}) \times (12.5 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \frac{325}{300}$$

$$+ (2 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times 2.303 \log \frac{4}{2}$$

$$= 13.53 \text{ J K}^{-1}$$

EXAMPLE 6.7 (SI units) Calculate the entropy changes for the fusion and vaporization of 1 mol of water at normal melting point (273 K) and boiling point (373 K). The molar enthalpy of fusion = 6.01 kJ mol^{-1} and the molar enthalpy of vaporization = 40.79 kJ mol^{-1}.

Solution Entropy change for fusion,

$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$$

$$\Delta H_{\text{fusion}} = 6.01 \text{ kJ mol}^{-1} = 6010 \text{ J mol}^{-1}$$

$$T_{\text{fusion}} = 273\ \text{K}$$

$$\therefore \quad \Delta S_{\text{fusion}} = \frac{6010\ \text{J mol}^{-1}}{273\ \text{K}} = 22.01\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Entropy change for vaporization,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

$$\Delta H_{\text{vap}} = 40.7\ \text{kJ mol}^{-1} = 40700\ \text{J mol}^{-1},$$

$$T_b = 373\ \text{K}$$

$$\therefore \quad \Delta S_{\text{vap}} = \frac{40700\ \text{J mol}^{-1}}{373\ \text{K}} = 109.1\ \text{J K}^{-1}\ \text{mol}^{-1}$$

EXAMPLE 6.8 A block of copper weighing 200 g is heated from 27°C to 127°C. What is the increase in its entropy if the average specific heat of copper over this range is taken to be equal to 0.09 cal g^{-1} K^{-1}.

Solution The entropy change

$$\Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T} = C_p \ln \frac{T_2}{T_1}$$

Specific heat = 0.09 cal $K^{-1}g^{-1}$

Heat capacity $C_p = 0.09 \times 200 = 18$ cal K^{-1}

$$T_1 = 273+27 = 300\ \text{K}, \qquad T_2 = 273+127 = 400\ \text{K}$$

$$\therefore \quad \Delta S = (18\ \text{cal K}^{-1}) \times 2.303 \log \frac{400}{300}$$

$$= 5.18\ \text{cal K}^{-1}$$

EXAMPLE 6.9 Calculate the entropy change for the conversion of 1 mol of α-tin (at 13°C, 1 atm) to 1 mol of β-tin (at 13°C, 1 atm), if the enthalpy of transition is 2.095 kJ mol^{-1}.

Solution The change in entropy during phase transition is

$$\Delta S = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}$$

$\Delta H_{\text{trans}} = 2.095 \times 1000\ \text{J mol}^{-1}$,

$T_{\text{trans}} = 13+273 = 286\ \text{K}$

$$\Delta S = \frac{2.095 \times 1000}{286} = 7.32\ \text{J K}^{-1}\ \text{mol}^{-1}$$

6.6 ENTROPY CHANGE IN CHEMICAL REACTIONS

The entropy change of a chemical reaction is given by the difference between the sum of entropies of all the products and the sum of entropies of all the reactants. For example, for the reaction,

$$aA + bB + \ldots = lL + mM + \ldots$$

$$\Delta S = (l\, S_L + m\, S_M + \ldots) - (a\, S_A + b\, S_B + \ldots)$$

or

$$\Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$$

The entropy of 1 mol of a substance in the pure state at 1 atm pressure and 25°C is called the *standard entropy* of the substance, and is denoted as $S°$. Thus,

$$\Delta S° = \Sigma S°_{\text{products}} - \Sigma S°_{\text{reactants}}$$

6.7 PHYSICAL MEANING OF ENTROPY

Entropy is regarded as a measure of the degree of disorder (or randomness) of a system. The relation between entropy and disorder provides a suitable explanation for entropy changes in various processes. In isothermal expansion of an ideal gas, although the energy remains constant, the entropy increases due to increasing disorder because the molecules now have much more space to move around. Similarly, mixing of two ideal gases at a given temperature leads to increase of disorder or entropy.

EXAMPLE 6.10 Calculate the entropy change for the reaction,

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

at 25°C, given that the standard entropies of gaseous hydrogen, gaseous oxygen and liquid water are 130.6, 205.1 and 70 J K^{-1} mol^{-1}, respectively.

Solution The entropy change of a reaction is

$$\begin{aligned}\Delta S &= \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}\\ &= [2S°H_2O] - [2S°(H_2) + S°(O_2)]\\ &= (2 \times 70) - [2 \times 130.6 + 205.1]\\ &= -\,326.3 \text{ J K}^{-1}\end{aligned}$$

6.8 THE THIRD LAW OF THERMODYNAMICS

The third law of thermodynamics deals with the entropies of perfect crystalline substances at absolute zero of temperature. According to this law, the entropies of all pure crystalline solids may be taken as zero at the absolute zero of temperature.

It may be noted that this law is true only for substances which exist in the perfectly crystalline form at 0°K. However, if there are imperfections *of any type in the perfect crystalline arrangement at 0°K, then* the entropy will be larger than zero. The common limitations of the third law are noticed in the following cases:

(1) Glassy solids in which the arrangement is less regular than in crystalline solids, e.g. glassy glycerine at 0°K has an entropy greater than zero.

(2) Solids containing mixtures of isotopes, e.g., chlorine at 0°K exists as $Cl^{35}-Cl^{35}$, $Cl^{37}-Cl^{37}$ and $Cl^{35}-Cl^{37}$ molecules, and entropy of solid chlorine is not zero at 0°K.

(3) Crystals of pure substances which fail to attain perfect order at 0°K, e.g. CO, N_2O, NO (dimer N_2O_2), H_2O, etc.

The importance of this law lies in the fact that it helps to calculate the absolute entropies of pure substances at different temperatures. The entropy (S) of the substance at different temperature T may be calculated from the measurements of heat capacities (C_p) at a number of temperatures between 0°K and T°K, from the relation,

$$\Delta S = \int_0^T C_p\, d\ln T = 2.303 \int C_p\, d\log T$$

The integral can be evaluated by plotting C_p versus log T, measuring the area under the curve between $T = 0$ and $T = T$°K and multiplying by 2.303. If C_p is constant over the temperature range T_1 to T_2 K, then

$$\Delta S = C_p \ln \frac{T_2}{T_1} = 2.303\, C_p \log \frac{T_2}{T_1}$$

For liquids and gaseous substances, the total absolute entropy of the substance at a given temperature will be the sum of all the entropy changes which the substance has to undergo in order to reach that state, starting from a crystalline solid at absolute zero. For example, for a gas at 1 atm pressure and 25°C, it may be expressed as

$$\underset{T=0}{\text{Solid}} \xrightarrow{\Delta S_1 = \int_0^{T_f} C_p\,(\text{solid})\, d\ln T} \underset{\substack{T = T_f \\ \text{(fusion point)}}}{\text{Solid}} \xrightarrow[\text{entropy of fusion}]{\Delta S_2 = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}}$$

$$\underset{T=T_f}{\text{Liquid}} \xrightarrow{\Delta S_3 = \int_{T_f}^{T_b} C_p\,(\text{liquid})\, d\ln T} \underset{\substack{(T = T_b) \\ \text{boiling} \\ \text{point}}}{\text{Liquid}} \xrightarrow[\text{entropy of vaporization}]{\Delta S_4 = \frac{\Delta H_{\text{evap}}}{T_b}}$$

$$\underset{T=T_b}{\text{Gas}} \xrightarrow{\Delta S_5 = \int_{T_b}^{298} C_p\,(\text{gas})\, d\ln T} \underset{T = 298\text{K}}{\text{Gas}}$$

Thus,

$$S_{(T)} = \int_0^{T_f} C_p\,(\text{solid})\, d\ln T + \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} + \int_{T_f}^{T_b} C_p\,(\text{liquid})\, d\ln T$$

$$+\frac{\Delta H_{\text{evap}}}{T_b}+\int_{T_b}^{T} C_p\,(\text{gas})\; d\ln T$$

1. If the substance is solid at temperature T, only the first term is to be taken with $T_f = T$.

2. If the substance is liquid at temperature T, the first three terms are to be taken with $T_b = T$.

3. If the substance is gas, the full equation must be used.

4. If the solid involves polymorphic transition, another term, $\Delta H_{\text{trans}}/T_{\text{trans}}$ has to be included in the above expression.

EXAMPLE 6.11 Calculate the change in entropy when two moles of ice are heated from $-10°C$ to $10°C$, given that $C_{p,m}$ (ice) $= 37.7\ \text{J mol}^{-1}\ \text{K}^{-1}$, $C_{p,m}$ (water) $= 75.3\ \text{J mol}^{-1}\ \text{K}^{-1}$ and molar enthalpy of fusion $= 6.01\ \text{kJ mol}^{-1}$. (assume heat capacities to be constant in this temperature range).

Solution The total entropy change can be calculated in the following steps:

(a) Entropy change when 2 mol of ice are heated from $-$ 10°C (263 K) to 0°C (273 K):

$$\Delta S_1 = n\ C_{p,m} \ln \frac{T_2}{T_1}$$

$$n = 2\ \text{mol}, \quad C_{p,m} = 37.7\ \text{J mol}^{-1}, \quad T_2 = 273\ \text{K}, \quad T_1 = 263\ \text{K}$$

$$\Delta S_1 = (2\ \text{mol} \times 37.7\ \text{J mol}^{-1}\text{K}^{-1}) \times 2.303 \log \frac{273}{263}$$

$$= 2.81\ \text{J K}^{-1}$$

(b) Entropy change during melting of ice at 273 K

$$\Delta S_2 = \frac{\Delta H_f}{T_f} = \frac{(2\ \text{mol}) \times (6.01 \times 1000\ \text{J mol}^{-1})}{273}$$

$$= 44.03\ \text{J K}^{-1}$$

(c) Entropy change for heating water from 273 K to 283 K

$$\Delta S_3 = n\ C_{p,m} \ln \frac{T_2}{T_1}$$

$$= (2\ \text{mol}) \times (75.3\ \text{J K}^{-1}\text{mol}^{-1}) \times 2.303 \log \frac{283}{273}$$

$$= 5.42\ \text{J K}^{-1}$$

Total entropy change,

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$= 2.81 + 44.03 + 5.42 = 52.26\ \text{J K}^{-1}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 6.12 One mole of an ideal monoatomic gas, occupying 5 dm^3 at 327°C, is carried through a Carnot cycle. It is first expanded isothermally to a volume of 25 dm^3 and then adiabatically to a stage at which the temperature is 27°C. It is then compressed isothermally to a certain volume and finally back to the initial state. Calculate the quantities ΔU, q and w in each step. Also calculate the efficiency.

Solution The Carnot cycle may be considered in the following four steps:

Step 1. Isothermal expansion from volume 5 dm³ to 25 dm³

$$w = -\, nRT_1 \ln \frac{V_2}{V_1}$$

$n = 1$ mol, $R = 8.314 \text{ J K}^{-1}\text{mol}^{-1}$, $T_1 = 327+273 = 600$ K,
$V_1 = 5 \text{ dm}^3$, $V_2 = 25 \text{ dm}^3$

$$\therefore \quad w_1 = -\,(1 \text{ mol}) \times (8.314 \text{ J K}^{-1}\text{ mol}^{-1}) \times (600 \text{ K}) \times 2.303 \log 25/5$$
$$= -\, 8.030 \text{ kJ}$$

$$\Delta U_1 = 0 \qquad \text{and } q_1 = -w_1 = 8.030 \text{ kJ}$$

Step 2. Adiabatic expansion from 600 K to 27 + 273 (= 300) K

$$q_2 = 0, \qquad \Delta U_2 = C_V\,(T_2 - T_1)$$
$$C_{V,m} = \tfrac{3}{2} R \text{ (for monoatomic gas)} = \tfrac{3}{2} \times 8.314 \text{ J K}^{-1}\text{ mol}^{-1}$$
$$\Delta U_2 = \tfrac{3}{2} \times (8.314 \text{ J K}^{-1}\text{ mol}^{-1}) \times (300 - 600)$$
$$= -3.741 \text{ kJ}$$
$$w_2 = \Delta U_2 = -3.741 \text{ kJ}$$

Step 3. Isothermal compression at 300 K

$$w_3 = -\, RT_2 \ln \frac{V_4}{V_3}$$

V_3 corresponds to the volume in step 2, which may be calculated as follows:

For an adiabatic process, $V_2^{R/C_{V,m}}\, T_1 = V_3^{R/C_{V,m}}\, T_2$

or
$$\left(\frac{V_2}{V_3}\right)^{R/C_{V,m}} = \frac{T_2}{T_1}$$

$V_2 = 25 \text{ dm}^3$, $R/C_{V,m} = \dfrac{R \times 2}{3R}$, $T_2 = 300$ K, $T_1 = 600$ K

or
$$\left(\frac{25}{V_3}\right)^{2/3} = \frac{300}{600}$$
$$V_3 = 70.70 \text{ dm}^3$$

Similarly,
$$\left(\frac{V_4}{V_1}\right)^{2/3} = \frac{T_1}{T_2}$$
$$\left(\frac{V_4}{5}\right)^{2/3} = \frac{600}{300}$$
$$V_4 = 14.14 \text{ dm}^3$$

$$\therefore \qquad w_3 = -\,1 \times 8.314 \times 300 \times 2.303 \log \frac{14.14}{70.70}$$
$$= 4.015 \text{ kJ}$$

$$\Delta U_3 = 0, \qquad q_3 = -w_3 = -\,4.015 \text{ kJ}$$

Step 4. Adiabatic compression from 300 K to 600 K

$$q_4 = 0, \quad \Delta U_4 = C_V (T_2 - T_1)$$
$$= \tfrac{3}{2} \times 8.314 \times (600 - 300)$$
$$= 3.741 \text{ kJ}$$
$$w_4 = \Delta U_4 = 3.741 \text{ kJ}$$

Thus,

Total energy change, $\Delta U = 0 - 3.741 + 0 + 3.741 = 0$

Total work done, $w = -8.030 - 3.741 + 4.015 + 3.741$
$= -4.015$ kJ

Total heat absorbed, $q_2 = 8.030$ kJ

Efficiency $= \dfrac{-w}{q_2} = \dfrac{4.015}{8.030} = 0.5$

EXAMPLE 6.13 The entropies of vaporization of three liquids, and their corresponding boiling temperatures (T_b) at 1 atm, are

Liquid	ΔS_{evap}	T_b
CCl_4	86 J K^{-1} mol^{-1}	76.7°C
C_6H_6	87 J K^{-1} mol^{-1}	80.1°C
H_2O	109 J K^{-1} mol^{-1}	100°C

Arrange these liquids in decreasing order of their molar enthalpies of vaporization.

Solution Entropy change during vaporization is

$$\Delta S_{evap} = \frac{\Delta H_{evap}}{T_b}$$

or $$\Delta H_{evap} = \Delta S_{evap} \times T_b$$

For CCl_4,

$$\Delta S_{evap} = 86.0 \text{ J K}^{-1} \text{ mol}^{-1}, \quad T_b = (273 + 76.7) = 349.7 \text{ K}$$
$$\Delta H_{evap} (CCl_4) = (86.0 \text{ J K}^{-1} \text{ mol}^{-1}) \times (349.7 \text{ K}) = 30.074 \text{ kJ mol}^{-1}$$

For C_6H_6,

$$\Delta S_{evap} = 87.0 \text{ J K}^{-1} \text{ mol}^{-1}, \quad T_b = 273 + 80.1 = 353.1 \text{ K}$$
$$\Delta H_{evap} (C_6H_6) = (87.0 \text{ J K}^{-1} \text{ mol}^{-1}) \times (353.1 \text{ K}) = 30.720 \text{ kJ mol}^{-1}$$

For H_2O,

$$\Delta S_{evap} = 109 \text{ J K}^{-1} \text{ mol}^{-1}, \quad T_b = 100 + 273 = 373 \text{ K}$$
$$\Delta H_{evap} (H_2O) = (109 \text{ J K}^{-1} \text{ mol}^{-1}) \times (373 \text{ K}) = 40.657 \text{ kJ mol}^{-1}$$

Thus, the decreasing order of enthalpies of vaporization is

$$H_2O > C_6H_6 > CCl_4$$

EXAMPLE 6.14 The heat capacity at constant pressure of a certain substance is 0.203 kJ K^{-1} mol^{-1}, over the temperature range 327 to 527°C. The entropy at 327°C is 0.469 kJ K^{-1} mol^{-1}. Calculate the entropy per mole at 527°C.

Solution The change in entropy with temperature,

$$\Delta S = C_{V,m} \ln \frac{T_2}{T_1}$$

or $$S_{(800\ \mathrm{K})} - S_{(600\ \mathrm{K})} = C_{V,m} \ln \frac{T_2}{T_1}$$

$$S_{(600\ \mathrm{K})} = 0.469\ \mathrm{kJ\ K^{-1}\ mol^{-1}}, \quad T_2 = 800\ \mathrm{K}, \quad T_1 = 600\ \mathrm{K},$$

$$C_{V,m} = 0.203\ \mathrm{kJ\ K^{-1}\ mol^{-1}}$$

$$S_{(800\ \mathrm{K})} - (0.469\ \mathrm{kJ\ K^{-1}\ mol^{-1}}) = (0.203\ \mathrm{kJ\ K^{-1}\ mol^{-1}}) \times 2.303 \log \frac{800}{600}$$

$$= 0.058\ \mathrm{kJ\ K^{-1}\ mol^{-1}}$$

or $$S_{(800\ \mathrm{K})} = 0.058 + 0.469 = 0.527\ \mathrm{kJ\ mol^{-1}\ K^{-1}}$$

Example 6.15 One mole of water evaporates at 100°C and 1 atm pressure, by transferring heat from a source only infinitely greater than 100°C. Calculate the entropy changes in (i) the system and (ii) the surroundings. (Enthalpy of vaporization of water = 40.7 kJ mol^{-1}).

Solution Entropy change in the system during evaporation of water

$$\Delta S = \frac{\Delta H_{\mathrm{evap}}}{T_b}$$

$$\Delta H_{\mathrm{evap}} = 40.7\ \mathrm{kJ\ mol^{-1}}, \ T_b = 373\ \mathrm{K}$$

$$\Delta S_{\mathrm{system}} = \frac{40.7 \times 1000}{373} = 109\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

$$\Delta S_{\mathrm{surroundings}} = -\Delta S_{\mathrm{system}} = -109\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Example 6.16 Calculate the change in entropy when 100 g of hot water at 90°C are added to 100 g of water at 10°C in an insulated vessel. The molar heat capacity of water at constant pressure = 75.48 J K^{-1} mol^{-1}.

Solution Let the final temperature on mixing be T

Heat lost by hot water = Heat gained by cold water

Temperature of hot water = 273 + 90 = 363 K

Temperature of cold water = 273 + 10 = 283 K

or $$C_{p,m}(363 - T) = C_{p,m}(T - 283)$$

$$\frac{100}{18} \times 75.48\,(363 - T) = \frac{100}{18} \times 75.48\,(T - 283)$$

or $$T = 323\ \mathrm{K}$$

$$\Delta S = \Delta S_{\text{hot water}} + \Delta S_{\text{cold water}}$$

$$\Delta S_{\text{hot water}} = n\, C_{p,m} \ln \frac{T_2}{T_1}$$

$$= \left(\frac{100}{18}\ \mathrm{mol}\right) \times (75.48\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times 2.303 \log \frac{323}{363}$$

$$= -48.96\ \mathrm{J\ K^{-1}}$$

$$= -2.75 \text{ J K}^{-1}$$

$$\therefore \quad \Delta S = \Delta S_1 + \Delta S_2 = 2.81 - 2.75 = 0.06 \text{ J K}^{-1}$$

QUESTIONS

Numerical Problems

6.1 Calculate the maximum theoretical efficiency of a reversible heat engine operating between 20°C and 100°C.

6.2 An engine works between the temperatures 100°C and 200°C while another engine works between 150°C and 300°C. Which one is more efficient?

6.3 Calculate the maximum efficiency of a steam engine operating between 125°C and 25°C. What would be the efficiency of the engine if the boiler temperature is raised to 200°C, the temperature of the sink remaining the same?.

6.4 A reversible Carnot engine does work equivalent to 21 kJ per cycle. If the heat supplied in isothermal expansion is 70 kJ per cycle at 127°C, calculate (i) the efficiency of the engine and (ii) the temperature at which heat is rejected.

6.5 What will be the maximum amount of work required to operate a refrigerator which removes 500 cal of heat at 0°C and rejects it at 40°C?

6.6 Calculate the ratio of temperatures of the source and sink for a heat engine whose efficiency is 20 per cent.

6 7 (SI Units) Calculate the entropy change when 5 mol of an ideal gas expand isothermally and reversibly from a volume of 2 dm^3 to 20 dm^3 at 300 K.

6.8 (SI unit) Calculate the changes of entropy in the system and the surroundings when one mole of a perfect gas at room temperature expands from 1 dm^3 to 4 dm^3 in (a) an isothermal reversible manner and (b) an isothermal irreversible manner.

6.9 Calculate the increase in entropy if two moles of helium are heated from 27°C to 127°C at constant volume and at constant pressure.

6.10 One mole of helium is heated from 25°C to 200°C at a constant pressure of 1 atm. The absolute entropy of helium at 200°C is 32.3 cal deg^{-1} mol^{-1}. Calculate the absolute entropy of helium at 25°C.

6.11 Five moles of a perfect gas are heated from 27°C to 327°C at a constant pressure of 1 atm. Calculate the entropy change in (i) the system and (ii) the surroundings. The molar heat capacity of the gas is 23.5 J K^{-1}.

6.12 Calculate the increase in entropy of a mole of a perfect diatomic gas ($C_p = 7/2\,R$) at 25°C and 1 atm, in a container of 2 dm^3, when it is allowed to expand to 4 dm^3 and simultaneously heated to 65°C.

6.13 (SI Units) Calculate the entropy change for the condensation of one mole of ethyl alcohol at boiling point. The enthalpy of vaporization of ethyl alcohol is 38.6 kJ mol^{-1} and the boiling point is 351.5 K.

6.14 Calculate the entropy change when one mole of water is converted into one mole of steam, reversibly, at its boiling point. Latent heat of vaporization is 540 cal g^{-1}.

6.15 The boiling points of C_6H_6, CCl_4 and CH_3OH are 80.1, 76.7 and 64.2°C, respectively. Estimate the molar heats of vaporization of these.

6.16 Solid phosphine undergoes a phase change from β form to α form at −223°C, with the absorption of 777.0 J mol^{-1} of heat. Calculate the entropy change when 3 mol of β-phosphine are converted to α-phosphine.

6.17 Calculate the entropy changes for the following processes:

(a) 1 mole H_2O (l, 1 atm, 100°C) $\rightleftharpoons$ 1 mole H_2O (v, 1 atm, 100°C)
$\Delta H_{evap} = 9.75$ kcal mol^{-1}.

(b) 1 mole H_2O (s, 1 atm, 0°C) $\rightleftharpoons$ 1 mole H_2O (l, 1 atm, 0°C)
$\Delta H_{fus} = 1.44$ kcal mol^{-1}.

6.18 (SI Units) Two moles of a perfect gas, initially at standard temperature and pressure, expand isothermally and irreversibly to 89.6 dm^3. The work done on the system is -400 J. Calculate ΔS.

6.19 (SI Units) For a certain gas, $C_{p,m} = 20.78$ J mol^{-1} K^{-1}. Calculate the change in entropy undergone by 2 mol of the gas on being heated from 300 K to 600 K at (a) constant volume (b) constant pressure.

6.20 One mole of nitrogen and three moles of oxygen are mixed at 25°C. The final pressure is 760 torr. Calculate the entropy change for mixing, the initial pressure of each gas also being 760 torr.

6.21 Calculate the change in entropy when 2 moles of water at 90°C are mixed adiabatically with 3 moles of water at 40°C. Molar heat capacity of water = 75.5 J K^{-1} mol^{-1}.

6.22 What is the entropy change when 500 g of water at 80°C are added to 500 g of water at 10°C? C_p (H_2O) = 75.5 J K^{-1} mol^{-1}.

6.23 A block of copper weighing 200 g at 150°C is introduced in a thermos flask containing 200 g of water at 10°C. What is the final temperature of the system? What will be the change in entropy if the average specific heats of copper and water may be taken as 0.09 and 1.0 cal g^{-1} deg^{-1}. Assume that the water equivalent of the thermos flask is zero.

6.24 Two moles of an ideal monoatomic gas occupying 5 dm^3 at 500 K are carried through a Carnot cycle. It is first expanded isothermally to a volume of 10 dm^3 and then adiabatically to a stage at which temperature is 300 K. It is then compressed isothermally to a certain volume and, finally, back to its initial state. Calculate the quantities q, w, ΔU and efficiency.

6.25 The heat capacity of nitrogen may be expressed as

$$C_p = (28.58 + 0.00377\ T)\ \text{J K}^{-1}\ \text{mol}^{-1}$$

Calculate the entropy change when 1 mol of nitrogen is heated from 27°C to 127°C.

6.26 The entropy change for the formation of C_2H_5OH is -344.9 J K^{-1} mol^{-1}. Calculate the absolute entropy of ethanol, given that the entropies of carbon, hydrogen and oxygen are 5.8, 130.6 and 205.2 J K^{-1} mol^{-1}, respectively.

6.27 Calculate the entropy changes for the combustion of glucose and sucrose. The standard absolute entropies are

S° [CO_2] = 213.7 J K^{-1} mol^{-1}, S° [H_2O (l)] = 70.0 J K^{-1} mol^{-1}
S° [O_2] = 205.0 J K^{-1} mol^{-1}
S°[$C_6H_{12}O_6$] = 212.1 J K^{-1} mol^{-1}, S°[$C_{12}H_{22}O_{11}$] = 360.2 J K^{-1} mol^{-1}

6.28 Calculate the entropies of vaporization of the following from the data:

Substance	*Boiling point* (°C)	ΔH_{evap} (kJ mol^{-1})
Benzene	80.1	30.8
Water	100	40.7
Cyclohexane	80.7	30.1

6.29 Calculate the entropy change when helium at 25°C and 1 atm pressure in a container of volume 2 dm^3 is allowed to expand to 4 dm^3 and simultaneously heated to a temperature of 100°C.

6.30 The molar heat capacities of substances is expressed as
$C_{p,m}=a+bT+CT^{-2}$ where the values of a, b and c are

Substance	a	b	c
O_2	29.96	4.18×10^{-3}	-1.67×10^{-5}
CO	28.41	4.10×10^{-3}	-0.46×10^{-5}
CO_2	44.22	8.79×10^{-2}	-8.62×10^{-5}

Calculate the change in entropy of the following reaction:

$$2CO + O_2 \longrightarrow 2CO_2$$

from 27 to 127°C

QUIZ QUESTIONS

Type A: Multiple Choice

6.31 A process in which the system, after undergoing various processes, returns to its initial state is called a/an
(a) reversible process
(b) irreversible process
(c) cyclic process
(d) Hess's law

6.32 In the second step of the Carnot cycle, the gas is expanded adiabatically and reversibly from a volume V_2 to V_3 and the temperature falls from T_1 to T_2. The energy change (ΔU) during the process is
(a) $C_p\,(T_2-T_1)$
(b) zero
(c) $RT_2 \ln \frac{V_3}{V_2}$
(d) $C_V\,(T_2-T_1)$

6.33 The overall energy change (ΔU) during the Carnot cycle is
(a) equal to w
(b) zero
(c) maximum
(d) equal to q

6.34 In the Carnot cycle, a process is performed in which the gas is compressed reversibly and isothermally, from
P_3, V_3 and T_2 to P_4, V_4 and T_2
During this process
(a) $\Delta U = 0,\ q=w=RT_2 \ln \frac{V_4}{V_3}$
(b) $\Delta U = q,\ w = -\,RT_2 \ln \frac{V_4}{V_3}$
(c) $\Delta U = 0,\ q = RT_2 \ln \frac{V_4}{V_3}$ and $w = -\,RT_2 \ln \frac{V_4}{V_3}$
(d) $\Delta U = 0,\ q = RT_2 \ln \frac{V_4}{V_3}$

6.35 The ratio of the network done by the system during the cycle and the heat absorbed from a source is called
(a) useful work
(b) reversible work
(c) efficiency
(d) limiting work

6.36 The efficiency of a reversible heat engine depends only on the
(a) temperature of the heat source
(b) temperature of the heat sink

(c) nature of the engine fluid
(d) temperature of the heat source and the sink

6.37 If T_1 and T_2 are the temperatures of the heat source and sink, respectively, then efficiency of an engine may be expressed as

(a) $\dfrac{T_2}{T_1}$ (b) $\dfrac{T_2 - T_1}{T_2}$

(c) $\dfrac{T_1 - T_2}{T_1}$ (d) $1 + \dfrac{T_1}{T_2}$

6.38 All cyclic engines working reversibly between the same temperatures of source and sink have the same efficiency. This is the statement for the
(a) Carnot cycle
(b) efficient engine
(c) Carnot theorem
(d) second law of thermodynamics

6.39 Which of the following is not one of the statements of the second law of thermodynamics ?
(a) The entropy of the universe is always increasing.
(b) It is impossible to transfer heat from a heat source to a hotter body without doing some work.
(c) It is not possible to construct a perpetual motion machine which can work endlessly without the expenditure of energy.
(d) It is not possible to take heat from a source and convert all of it into work without losing some of it to a colder reservoir.

6.40 The entropy of the universe
(a) tends towards a maximum
(b) tends towards a minimum
(c) tends to be zero
(d) remains constant

6.41 In a reversible process,

$$\Delta S_{sys} + \Delta S_{surr} \text{ is}$$

(a) > 0
(b) < 0
(c) $\geqslant 0$
(d) $= 0$

6.42 If ΔH_{fus} is the latent heat of melting and T_{fus} is the melting point, then entropy of melting is

(a) $\dfrac{\Delta H_{fus}}{T_{fus}}$ (b) $T_{fus}/\Delta H_{fus}$

(c) $\Delta H_{fus} \times T_{fus}$ (d) $\Delta H_{fus} - T$

6.43 If heat is measured in joules, the units of entropy are
(a) joules
(b) joules per degree
(c) joules-degree per mol
(d) degree per joules

6.44 If p_1, T_1 represent the initial state and p_2, T_2 the final state of an ideal gas, then entropy change may be expressed as

(a) $\Delta S = C_p \ln \dfrac{T_2}{T_1} + R \ln \dfrac{p_2}{p_1}$

(b) $\Delta S = C_V \ln \dfrac{T_1}{T_2} - RT_2 \ln \dfrac{p_1}{p_2}$

(c) $\Delta S = C_p \ln \dfrac{T_2}{T_1} + R \ln \dfrac{p_1}{p_2}$

(d) $\Delta S = C_p \ \ln \dfrac{T_1}{T_2} - R \ln \dfrac{p_1}{p_2}$

6.45 In an isobaric process, when temperature changes from T_1 to T_2, ΔS is equal to

(a) $2.303 \ C_p \ \log \dfrac{T_2}{T_1}$

(b) $2.303 \ C_p \ \ln \dfrac{T_2}{T_1}$

(c) $2.303 \ C_p \ \log \dfrac{T_1}{T_2}$

(d) $C_p \ \log \dfrac{T_2}{T_1}$

6.46 Entropy change for an adiabatic reversible process is
(a) positive
(b) zero
(c) negative
(d) positive or zero

6.47 Which of the following is the correct statement of the third law of thermodynamics ?
(a) Entropy of all pure crystalline solids may be taken as zero at absolute zero of temperature.
(b) Entropy of all pure crystalline solids may be taken as unity at absolute zero of temperature.
(c) The standard state for a solid is the pure state of solid at 1 atm pressure and its activity is unity.
(d) Spontaneous processes are accompanied by increase in entropy as well as increase in the disorder of the system.

6.48 Which of the following is not correct

(a) $\left(\dfrac{\partial H}{\partial S}\right)_p = T$

(b) $\left(\dfrac{\partial U}{\partial S}\right)_V = -T$

(c) $\left(\dfrac{\partial U}{\partial V}\right)_S = -p$

(d) $\left(\dfrac{\partial H}{\partial p}\right)_S = V$

6.49 According to the third law of thermodynamics, the entropy at 0°K. is zero for
(a) elements in their stable form
(b) perfectly crystalline solids
(c) substances at 1 atm and 25°C
(d) N_2O

6.50 For which one of the following cases is $\Delta S = \Delta H/T$
(a) an adiabatic process
(b) a process for which

$$\Delta C_p = 0$$

(c) an isothermal reversible phase change
(d) a process at constant pressure

Type B: Multiple Choice (Numerical Problems)

6.51 A steam engine is operated by taking steam at 127°C and rejecting it at 37°C. What is the maximum efficiency attainable by the engine ?
(a) 25.0%
(b) 22.5%
(c) 28.2%
(d) 70.8%

6.52 Four engines, *A*, *B*, *C* and *D*, take steam at 130°C and reject it at 20°, 30°, 37° and 45°C, respectively. Which of these is most efficient ?

(a) *A*
(b) *B*
(c) *C*
(d) *D*

6.53 An engine works between the temperatures 27°C and 127°C. Which of the following statements is correct, if all the engines work reversibly ?

(a) It is less efficient than an engine working between 310°K and 400°K.
(b) It is more efficient than an engine working between 17°C and 127°C.
(c) It is more efficient than engines working between 310–410°K and 290–400°K.
(d) It is more efficient than an engine working between 127°C and 227°C.

6.54 The amount of heat supplied to a Carnot cycle working between 27°C and 127°C, if the maximum work obtained is 210 cal is

(a) 52 cal
(b) 840 cal
(c) 420 cal
(d) 52.5 cal

6.55 The entropy change for the fusion of 1 mol of a solid which melts at 27°C is (latent heat of fusion = 600 cal mol^{-1})

(a) 2 cal deg^{-1}
(b) 22.2 cal deg^{-1}
(c) 180 kcal deg
(d) 0.5 cal^{-1} deg

6.56 Two moles of an ideal gas expand reversibly from a volume of 5 to 50 *l* at 27°C. The change in entropy is ($R = 2$ cal mol^{-1} K^{-1})

(a) 4 cal
(b) 9.2 cal
(c) 2.303 cal
(d) 92.2 cal

6.57 The standard entropies of Ag(s), O_2(g) and Ag_2O(s) are 10.2, 49.0 and 29.0 cal mol^{-1}, respectively. The entropy change for the reaction at 298 K

$$Ag_2O(s) \longrightarrow 2Ag(s) + \tfrac{1}{2} O_2(g)$$ is

(a) 15.9 cal K^{-1}
(b) – 15.9 cal K^{-1}
(c) – 8.6 cal K^{-1}
(d) 25.9 cal K^{-1}

6.58 The latent heat of vaporization of water at 100°C is 540 cal g^{-1}. Calculate the entropy increase when one mole of water at 100° is evaporated.

(a) 26 cal K^{-1} mol^{-1}
(b) 1.82 cal K^{-1} mol^{-1}
(c) 367 cal K^{-1} mol^{-1}
(d) 540 × 18 cal K^{-1} mol^{-1}

6.59 The heat supplied to a Carnot engine is 400 k cal. The useful work done by the engine operating between 27°C and 127°C, is (1 cal = 4.185 J).

(a) 4.185×10^4 J
(b) 2.38×10^4 J
(c) 4.185×10^5 J
(d) 2.38×10^9 J

6.60 Consider the following data

$S^\circ_{H_2} = 31.21$ cal mol^{-1} deg^{-1}

$S^\circ_{C} = 1.36$ cal mol^{-1} deg^{-1}

$S^\circ_{O_2} = 49.0$ cal mol^{-1} deg^{-1}

$S^\circ_{CH_3OH}$ = 38.4 cal mol^{-1} deg^{-1}

What will be the entropy change for the formation of 1 mol of methyl alcohol from its elements ?

(a) 120.9 cal mol^{-1} deg^{-1}
(b) − 82.5 cal mol^{-1} deg^{-1}
(c) — 43.2 cal mol^{-1} deg^{-1}
(d) 47.6 cal mol^{-1} deg^{-1}

Type C: True or False

6.61 Absolute entropy of a solid is always zero.
6.62 Entropy is a measure of disorder of a system.
6.63 The first law of thermodynamics is inadequate to predict the spontaneity of a process.
6.64 Two reversible engines operating between the same temperatures are equally efficient.
6.65 The entropy of the universe remains constant.
6.66 The entropy of a perfectly crystalline solid at 0°K is unity.
6.67 In a reversible process, the entropy of the system and surroundings tends to increase.
6.68 The mixing of two ideal gases at a given temperature leads to increase in disorder and entropy.
6.69 For all reversible adiabatic processes, ΔS is zero.
6.70 In an irreversible process, the sum of the entropies of the system and the surroundings is zero.
6.71 At constant U, V and T, $\Delta S > 0$ represents the criterion for spontaneity.
6.72 The decrease in entropy is equal to the network done by the system, reversibly.
6.73 In a cyclic process, the overall change is zero.
6.74 The efficiency of an engine depends upon the temperature of the source, sink and engine fluid.
6.75 Entropy is an extensive property.

Type D: Fill in the blanks

6.76 The third law of thermodynamics states that the entropy of any pure perfect crystalline substance is zero at————.
6.77 An example of a reversible cyclic process is————.
6.78 The entropy of an isolated system tends to————.
6.79 Entropy is related to————.
6.80 The maximum work is done by a system in————manner.
6.81 The second law of thermodynamics introduces the concept of————.
6.82 The fraction of the heat absorbed by a system, which it can transform into work, is called————.
6.83 The heat absorbed or lost isothermally and reversibly, divided by the temperature at which the heat is absorbed or lost, is called————.
6.84 The process of condensation is accompanied by————of entropy.
6.85 The vaporization of a liquid is accompanied by————in entropy.

ANSWERS

Numerical Problems

6.1 0.21 *6.2* Efficiency of the first engine = 0.21; Second engine = 0.26; Second engine is more efficient *6.3* 0.25 and 0.37 *6.4* (i) 0.3 (ii) 7°C *6.5* Calculate efficiency $= 0.1278$, efficiency $= -\dfrac{w}{q_2}$; Work required, $-w = 639$ cal *6.6* Efficiency of the engine $= \dfrac{T_1 - T_2}{T_1} = 0.20$; $\dfrac{T_1}{T_2} = 1.25$ *6.7* 22.88 cal deg^{-1} *6.8* (a) $\Delta S_{\text{sys}} = 11.53$ J K^{-1}, $\Delta S_{\text{surr}} = -11.53$ J K^{-1}, (b) $\Delta S_{\text{sys}} = 11.53$ J K^{-1}, $\Delta S_{\text{surr}} = 0$, *6.9* 12.74 J K^{-1}, 21.23 J K^{-1} *6.10* 30.01 cal deg^{-1} *6.11* (i) 81.44 J K^{-1} (ii) $-$ 81.44 J K^{-1} *6.12* 9.43 J K^{-1} *6.13* $\Delta S_{\text{evap}} = 109.8$ J K^{-1} mol^{-1}, Now $\Delta S_{\text{condensation}} = -\Delta S_{\text{evap}} = -109$ J K^{-1} mol^{-1} *6.14* 26 cal K^{-1} mol^{-1} *6.15* Using Trouton's rule $\Delta H_v/T_b \approx 21$; 7.415, 7.344, 7.081 kcal mol^{-1} *6.16* 46.62 J K^{-1} *6.17* 26.14 cal K^{-1} mol^{-1}, 5.27 cal K^{-1} mol^{-1}, 5.27 cal K^{-1} mol^{-1} *6.18* 11.53 J K^{-1} *6.19* 17.28 J K^{-1}, 28.81 J K^{-1} *6.20* 18.66 J K^{-1} *6.21* Calculate the final temperature on mixing $T = 60°\text{C}$, using the relation, Heat gained = Heat lost, $\Delta S = \Delta S(\text{hot water}) + \Delta S(\text{cold water}) = 1.01$ J K^{-1} *6.22* 25.57 J K^{-1} *6.23* 1.49 cal deg^{-1} *6.24* $\Delta U_1 = 0$, $q_1 = -w_1 = 5.764$ kJ; $q_2 = 0$, $\Delta U_2 = w_2 = -4.988$ kJ; $\Delta U_3 = 0$, $q_3 = -w_3 = -3.457$ kJ; $q_4 = 0$, $\Delta U_4 = w_4 = 4.988$ kJ, Efficiency = 0.40 *6.25* 13.85 J K^{-1} *6.26* 161.1 J K^{-1} mol^{-1} *6.27* 260.1 J K^{-1}, 514.2 J K^{-1} *6.28* 87.23, 109.1, 85.1 J K^{-1} *6.29* Calculate the number of moles from initial conditions, $n = 0.08$, $\Delta S = 0.68$ J K^{-1} *6.30* 4.1283

Quiz Questions

6.31 (c) *6.32* (d) *6.33* (b) *6.34* (a) *6.35* (c) *6.36* (d) *6.37* (c) *6.38* (c) *6.39* (c) *6.40* (a) *6.41* (d) *6.42* (a) *6.43* (b) *6.44* (c) *6.45* (a) *6.46* (b) *6.47* (a) *6.48* (b) *6.49* (b) *6.50* (a) *6.51* (a) *6.52* (a) *6.53* (d) *6.54* (b) *6.55* (a) *6.56* (b) *6.57* (a) *6.58* (a) *6.59* (c) *6.60* (b) *6.61* False: The entropies of all pure crystalline solids may be taken as zero only at the absolute zero of temperature (third law of thermodynamics). *6.62* True *6.63* True *6.64* True *6.65* False *6.66* False : is assumed to be zero *6.67* False *6.68* True *6.69* True *6.70* False *6.71* True *6.72* False *6.73* True *6.74* False *6.75* True *6.76* absolute zero *6.77* Carnot cycle *6.78* increase *6.79* disorder *6.80* reversible manner *6.81* entropy *6.82* efficiency *6.83* entropy *6.84* decrease *6.85* increase

7

Free Energy Functions and their Applications

The feasibility of and condition for chemical equilibrium can be derived on the basis of energy, enthalpy and entropy. However, these require certain constraints on the systems, which are not normally maintained under laboratory conditions. For this purpose, two new functions viz., Helmholtz and Gibbs free energy functions, are defined. These predict the feasibility and equilibrium conditions at constant temperature and at constant volume or pressure and, therefore, are convenient for day-to-day use. They are commonly called free energy functions.

7.1 FREE ENERGY FUNCTIONS

Free energy functions are defined by the relations,

Helmholtz free energy, $A = U - TS$ (7.1)

Gibbs free energy, $G = H - TS$ (7.2)

The properties U, H and S depend only upon the state of the system. Therefore, A and G are also state functions. It can be shown that, at constant temperature,

(i) Decrease in Helmholtz free energy is equal to the amount of reversible work done by the system

$$- dA = \partial w_{\text{rev}} \tag{7.3}$$

(ii) Decrease in Gibbs free energy is equal to network (excluding expansion work) done ($\partial w_{\text{rev}} - pdV$) by the system in a reversible way,

$$- dG = \partial w_{\text{rev}}\,(\text{net}) = \partial w_{\text{rev}} - pdV \tag{7.4}$$

The changes in A and G when the system goes from state 1 to state 2, at constant T, are expressed by

$$\Delta A = \Delta U - T\Delta S \tag{7.5}$$

$$\Delta G = \Delta H - T\Delta S \tag{7.6}$$

7.2 CHANGES IN *U*, *H*, *A* AND *G* IN REVERSIBLE PROCESSES

The quantities U, H, A and G are related to other thermodynamic variables by the following equations:

$$dU = TdS - pdV \text{ so } \left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -p$$

Hence, $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{7.7}$$

$$dH = TdS + Vdp$$

so $$\left(\frac{\partial H}{\partial S}\right)_p = T, \quad \left(\frac{\partial H}{\partial p}\right)_S = V$$

Hence, $$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \tag{7.8}$$

$$dA = -pdV - SdT$$

So $$\left(\frac{\partial A}{\partial V}\right)_T = -p, \quad \left(\frac{\partial A}{\partial T}\right)_V = -S$$

Hence, $$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{7.9}$$

$$dG = Vdp - SdT$$

So $$\left(\frac{\partial G}{\partial T}\right) = V, \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

Hence, $$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \tag{7.10}$$

7.3 CRITERIA OF SPONTANEITY IN TERMS OF FUNCTIONS *U*, *H*, *S*, *A* AND *G*

The criteria of spontaneity in terms of U, H, S, A and G are

(i) $dU \leqslant 0$ (at constant S and V) (7.11)
(ii) $dH \leqslant 0$ (at constant S and p) (7.12)
(iii) $dS \geqslant 0$ (at constant U and V)
(iv) $dA \leqslant 0$ (at constant V and T) (7.13)
(v) $dG \leqslant 0$ (at constant p and T) (7.14)

It may be noted that the Gibbs free energy change is an important criterion for the spontaneity of a reaction or a process, and consists of enthalpic and entropic factors (Eq. 7.6). In some cases, both the enthalpy and entropy factors may favour the process, e.g. if ΔH is $-$ve and ΔS is $+$ve, then ΔG $(\Delta H - T\Delta S)$ is negative and the process is favoured. In other reactions, enthalpy and entropy factors may oppose each other, e.g. ΔH is $-$ve, ΔS is $-$ve and the sign of ΔG will be determined by the magnitudes of ΔH and ΔS.

EXAMPLE 7.1 (SI Units) Calculate the standard Gibbs free energy change at 298° K for the reaction

$$\text{C(graphite)} + \text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)}$$

Given that $\Delta H^\circ = -393.4 \text{ kJ mol}^{-1}$

$\Delta S^\circ = 2.9 \text{ J K}^{-1} \text{ mol}^{-1}$

Predict whether the reaction is spontaneous or not.

Solution The Gibbs free energy change ΔG° is expressed as

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\Delta H^\circ = -393.4 \text{ kJ mol}^{-1}, \qquad \Delta S^\circ = 2.9 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta G^\circ = -393.4 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (2.9 \times 10^{-3} \text{ kJ mol}^{-1})$$

$$= -394.3 \text{ kJ mol}^{-1}$$

As ΔG° is negative, the reaction is *spontaneous.*

Example 7.2 Calculate $(\Delta G - \Delta A)$ for the reaction

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l) \text{ at } 300 \text{ K}$$

Solution

$$\Delta G = \Delta H - \Delta(TS)$$

$$\Delta A = \Delta U - \Delta(TS)$$

$$\Delta G - \Delta A = \Delta H - \Delta U = \Delta U + \Delta(pV) - \Delta U = \Delta(pV)$$

or

$$\Delta G - \Delta A = \Delta n\, RT \qquad (\Delta pV = \Delta n\, RT \text{ for ideal gases})$$

$$\Delta n = 1 - (2 + 1) = -2, \qquad R = 8.314 \text{ J mol}^{-1}\text{K}^{-1},$$

$$T = 300 \text{ K}$$

$$\therefore \quad \Delta G - \Delta A = (-2 \text{ mol}) \times (8.314 \text{ J mol}^{-1}\text{K}^{-1}) \times (300 \text{ K})$$

$$= -4988.4 \text{ J.}$$

7.4 GIBBS FREE ENERGY CHANGE AND GIBBS FREE ENERGY OF FORMATION

It is not possible to determine the absolute values of the Gibbs free energy as the absolute values of H and U are unknown. Therefore, as in the case of enthalpy, the Gibbs free energy of elements (in their most stable form) are arbitrarily fixed equal to zero at one atmospheric pressure* at a specified temperature. The free energy changes for elements at any other temperature or pressure are measured with respect to this reference. For compounds, standard Gibbs free energy of formation is defined as the free energy change when one mole of the substance is formed at 1 atm from the elements in their standard states at the specified temperature. This is denoted by ΔG_f°. The values of the standard free energy of formation of various compounds help in determining the free energy change for various reactions at standard conditions,

$$\Delta G^\circ = \Sigma\, (\Delta G_f^\circ)_{\text{products}} - \Sigma(\Delta G_f^\circ)_{\text{reactants}}$$

Example 7.3 Calculate the standard Gibbs free energy changes from the free energies of formation data for the following reactions:

(a) $C_6H_6(l) + 7.5\ O_2(g) \longrightarrow 6\ CO_2(g) + 3H_2O(g)$.

Given that $\Delta G_f^\circ[C_6H_6(l)] = 172.8 \text{ kJ mol}^{-1}$

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*IUPAC, now recommends the pressure as 1 bar. But the values do not differ significantly as 1 atm = 1.01 bar

$$\Delta G^\circ_f\,[CO_2(g)] = -394.4 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ_f\,[H_2O(g)] = -228.6 \text{ kJ mol}^{-1}$$

(b) $Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$
Given that

$$\Delta G^\circ_f\,[Fe_2O_3(s)] = -741.0 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ_f\,[H_2O(l)] = -237.2 \text{ kJ mol}^{-1}$$

Solution We know that

$$\Delta G^\circ = \Sigma\,(G^\circ_f)_{\text{products}} - \Sigma\,(\Delta G^\circ_f)_{\text{reactants}}$$

(a) For the reaction

$$C_6H_6(l) + 7.5\ O_2(g) \longrightarrow 6\ CO_2(g) + 3H_2O(g)$$

$$\begin{aligned}\Delta G^\circ &= [6\Delta G^\circ_f(CO_2) + 3\ \Delta G^\circ_f(H_2O)] - [\Delta G^\circ_f(C_6H_6) + 7.5\ \Delta G^\circ_f(O_2)] \\ &= 6 \times (-394.4) + 3 \times (-228.6) - 172.8 - 0 \\ &= -3225 \text{ kJ}\end{aligned}$$

(b) For the reaction

$$Fe_2O_3(s) + 3H_2(g) \longrightarrow 2Fe(s) + 3H_2O(l)$$

$$\begin{aligned}\Delta G^\circ &= [2\ \Delta G^\circ_f(Fe) + 3\ \Delta G^\circ_f\, H_2O)] - [\Delta G^\circ_f(Fe_2O_3) + 3\ \Delta G^\circ_f(H_2)] \\ &= 2 \times 0 + 3 \times (-237.2) - (-741.0) - 0 \\ &= 29.4 \text{ kJ}\end{aligned}$$

EXAMPLE 7.4 Calculate the standard free energy change for the combustion of α-D-glucose,

$$C_6H_{12}O_6(s) + 6O_2(g) \longrightarrow 6\ CO_2(g) + 6H_2O(l)$$

Given that

$$\Delta H^\circ_f(C_6H_{12}O_6) = -1274.5 \text{ kJ mol}^{-1},$$

$$\Delta H^\circ_f(CO_2) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta H^\circ_f(H_2O) = -285.8 \text{ kJ mol}^{-1}$$

$S^\circ(C_6H_{12}O_6) = 212.1$ EU, $S^\circ(O_2) = 205.0$ EU,
$S^\circ(CO_2) = 213.6$ EU, $S^\circ(H_2O) = 69.9$ EU

Solution ΔG° can be calculated as

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$\begin{aligned}\Delta H^\circ &= 6\ \Delta H^\circ_f(CO_2) + 6\ \Delta H^\circ_f(H_2O) - [\Delta H^\circ_f(C_6H_{12}O_6) + 6\Delta H^\circ_f(O_2)] \\ &= 6 \times (-393.5) + 6 \times (-285.8) - [1 \times (-1274.5) + 0]\end{aligned}$$

$$[\because\ \Delta H^\circ_f(O_2) = 0]$$

$$= -2801.3 \text{ kJ}$$

$$\Delta S^\circ = 6\, S^\circ(CO_2) + 6S^\circ(H_2O) - [S^\circ(C_6H_{12}O_6) + S^\circ(O_2)]$$

$$= (6 \times 213.6) + (6 \times 69.9) - [1 \times 212.1 + 6 \times 205.0]$$

$$= 258.9 \text{ EU or } 258.9 \text{ J K}^{-1} \qquad [\text{EU} = \text{J K}^{-1}]$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -2801.3 \text{ kJ} - (298 \text{ K}) \times (258\ 9 \times 10^{-3} \text{ kJ K}^{-1})$$

$$= -2878.45 \text{ kJ}$$

EXAMPLE 7.5 Consider the reaction

$$4\ NH_3(g) + 5\ O_2(g) \longrightarrow 4\ NO(g) + 6H_2O(1) \qquad \Delta G^\circ = -241.8 \text{ kcal}$$

Calculate ΔG_f° [NO(g)] if $\Delta G_f^\circ(NH_3) = -3.9$ kcal mol^{-1} and

$$\Delta G_f^\circ(H_2O) = -56.7 \text{ kcal mol}^{-1}.$$

Solution For the reaction

$$4NH_3(g) + 5\ O_2(g) \longrightarrow 4NO(g) + 6H_2O(1)$$

$$\Delta G^\circ = 4\ \Delta G_f^\circ(NO) + 6\ \Delta G_f^\circ(H_2O) - [4\ \Delta G_f^\circ(NH_3) + 5\ \Delta G_f^\circ(O_2)]$$

$$\Delta G^\circ = -241.8 \text{ kcal}, \qquad \Delta G_f^\circ(NH_3) = -3.9 \text{ kcal mol}^{-1},$$

$$\Delta G_f^\circ(H_2O) = -56.7 \text{ kcal mol}^{-1}$$

$$-241.8 = 4 \times \Delta G_f^\circ(NO) + 6 \times (-56.7) - 4 \times (-3.9) - 5 \times 0$$

$$[\because \Delta G_f^\circ(O_2) = 0]$$

$$\text{or } 4\Delta G_f^\circ(NO) = -241.8 + 340.2 - 15.6$$

$$= 82.8 \text{ kcal}$$

$$\Delta G_f^\circ(NO) = \frac{82.8}{4} = 20.7 \text{ kcal}$$

7.5 DEPENDENCE OF *G* ON TEMPERATURE

The Gibbs free energy, *G* is

$$G = H - TS$$

Now, $dG = Vdp - SdT$

$$\therefore \quad \left(\frac{\partial G}{\partial T}\right)_p = -S$$

Substituting in the above relation, we obtain

$$\text{or} \qquad G = H + T\left(\frac{\partial G}{\partial T}\right)_p$$

$$\text{or} \qquad -S = \left(\frac{\partial G}{\partial T}\right)_p = \frac{G - H}{T}$$

Differentiating G/T with respect to T,

$$\frac{\partial(G/T)}{\partial T} = \frac{T\left(\frac{\partial G}{\partial T}\right) - G}{T^2} = -\frac{(G+TS)}{T^2}$$

$$\frac{\partial(G/T)}{\partial T} = -\frac{H}{T^2} \qquad (7.15)$$

This is called the Gibbs Helmholtz equation. For a given process, ΔG may be expressed as

$$\frac{\partial(\Delta G)}{\partial T} = -\Delta S$$

and $$\frac{\partial(\Delta G/T)}{\partial T} = -\frac{\Delta H}{T^2} \qquad (7.16)$$

Similarly, at constant volume, the equations, in terms of Helmholtz free energy, are

$$\Delta A = \Delta U + T\left[\frac{\partial \Delta A}{\partial T}\right]_V$$

and $$\frac{\partial(\Delta A/T)}{\partial T} = -\frac{\Delta U}{T^2} \qquad (7.17)$$

Example 7.6 (SI Unit) The Gibbs free energy values of a reaction at 300 K and 310 K are -121 kJ and -123.5 kJ, respectively. Determine its ΔH and ΔS in this temperature range.

Solution $\Delta G = \Delta H - T\Delta S$

$$-\Delta S = \frac{\partial \Delta G}{\partial T} = \frac{\Delta G(310) - \Delta G(300)}{310 - 300} = \frac{-123.5 - (-121.0)\text{ kJ}}{10\text{ K}}$$

$$= -0.25\text{ kJ K}^{-1}$$

$$\therefore \quad \Delta S = 0.25\text{ kJ K}^{-1}$$

At 300 K, $\Delta G = \Delta H - T\Delta S$

$$-121\text{ kJ} = \Delta H - (300\text{ K}) \times (0.25\text{ kJ K}^{-1})$$

$$\therefore \quad \Delta H = -121\text{ kJ} + 75\text{ kJ}$$

$$= -46\text{ kJ}$$

Example 7.7 ΔG for a reaction at 300° K is -16 kcal. ΔH for the reaction is -10 kcal. What is the entropy of the reaction and what will be ΔG at 330 K?

Solution $\Delta G = \Delta H - T\Delta S$

or $$\Delta S = \frac{\Delta H - \Delta G}{T}$$

$$\Delta H = -10\text{ kcal}, \qquad \Delta G = -16\text{ kcal}$$

$$\therefore \quad \Delta S = \frac{-10 + 16}{300} = 20 \times 10^{-3}\text{ kcal K}^{-1} = 20\text{ cal K}^{-1}$$

At 330 K,

$$\Delta G = \Delta H - T\Delta S$$

$$= -10\text{ kcal} - (330\text{ K}) \times (20 \times 10^{-3}\text{ kcal K}^{-1})$$

$$= -16.6\text{ kcal}$$

7.6 DEPENDENCE OF *G* ON PRESSURE

$$dG = Vdp - SdT$$

The Gibbs free energy depends on pressure. At constant temperature,

$$\left(\frac{\partial G}{\partial p}\right)_T = V$$

or $$dG = Vdp$$

The change in Gibbs free energy, when pressure changes from p_1 to p_2, may be expressed as

$$\Delta G = G_2 - G_1 = \int_{p_1}^{p_2} Vdp$$

For an ideal gas, p and V are related as

$$V = \frac{nRT}{p} \qquad \text{(for } n \text{ moles of the gas)}$$

so that $$\Delta G = \int_{p_1}^{p_2} \frac{nRT}{p} dp$$

or $$\Delta G = nRT \ln \frac{p_2}{p_1} \tag{7.18}$$

For real gases, V or dp are substituted from suitable equations of state.

For liquids and solids, the volumes may be considered almost constant because they are only slightly compressible. The free energy change may be expressed as

$$\Delta G = \int_{p_1}^{p_2} Vdp \doteq V(p_2 - p_1) \tag{7.19}$$

The free energy changes with pressure for solids and liquids are very small as compared to those in gases, and are generally neglected over a small pressure range, at any temperature unless the pressure change is extremely large.

EXAMPLE 7.8 Three moles of an ideal gas at 27°C and 1 atm are compressed isothermally until the final pressure becomes 5 atm. Calculate the Gibbs free energy change for this process.

Solution For isothermal compression,

$$\Delta G = nRT \ln \frac{p_2}{p_1}$$

$$n = 3 \text{ mol}, \qquad T = 27 + 273 = 300 \text{ K},$$
$$R = 8.314 \text{ J K}^{-1} \text{mol}^{-1},$$
$$p_1 = 1 \text{ atm}, \qquad p_2 = 5 \text{ atm}$$

$$\Delta G = (3\ \text{mol}) \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K}) \times 2.303 \log \frac{5}{1}$$

$$= 12.045\ \text{kJ}$$

EXAMPLE 7.9 (SI Units) One mole of an ideal gas is expanded isothermally from 0.01 dm³ to 0.10 dm³ at 300 K. Calculate ΔG.

Solution $\Delta G = nRT \ln \frac{p_2}{p_1} = nRT \ln \frac{V_1}{V_2}$

$$n = 1\ \text{mol}, \quad R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}, \quad T = 300\ \text{K},$$

$$V_1 = 0.01\ \text{dm}^3, \quad V_2 = 0.1\ \text{dm}^3$$

$$\Delta G = (1\ \text{mol}) \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K}) \times 2.303 \log \frac{0.01}{0.1}$$

$$= -\ 5744.1\ \text{J}$$

7.7 PARTIAL MOLAR QUANTITIES AND CHEMICAL POTENTIAL

The partial molar quantity of a component is defined as the change in extensive property of a mixture when one mole of the pure component is added, in such a way that there is no change in temperature, pressure and composition.

Partial molar quantities are of particular use when dealing with solutions. These are represented with a bar on the symbol. These can be defined mathematically as,

$$\bar{X}_i = \left(\frac{\partial X}{\partial n_i}\right)_{p,\, T,\, n_1,\, n_2,\, \ldots,\, n_j}$$

where $\bar{X}_i$ represents the partial molar quantity of component 'i'. (Here X is an extensive property such as V, U, H, S, A, G.) The subscripts $n_1, n_2 \ldots n_j$ imply that all these variables except n_i are constant. If we consider Gibbs free energy as the extensive property, then

$$G = f(p, T, n_1, n_2, \ldots, n_j)$$

Total change in G by small changes in all variables,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p,\, n_1,\, n_2,\, \ldots,\, n_j} dT + \left(\frac{\partial G}{\partial p}\right)_{T,\, n_1,\, n_2,\, \ldots,\, n_j} dp + \left(\frac{\partial G}{\partial n_1}\right)_{p,\, T,\, n_2,\, \ldots,\, n_j} dn_1 + \ldots \left(\frac{\partial G}{\partial n_j}\right)_{p,\, T,\, n_1,\, n_2,\, \ldots,} dn_j$$

The quantity $\left(\frac{\partial G}{\partial n_i}\right)_{p,\, T,\, n_1,\, n_2,\, \ldots,\, n_j}$ represents the partial molar free energy G_i of the substance 'i'. This is a very important quantity in physical chemistry and is also known as the *chemical potential*, represented by the symbol μ (Greek mu).

Thus, chemical potential may be defined as the change in free energy of a substance when one mole of it is added to such a large quantity of the system that there is no appreciable change in the overall composition of the system, at constant temperature and pressure. At constant T and p

$$(dG)_{T,\,p} = \mu_1\, dn_1 + \mu_2\, dn_2 + \ldots + \mu_j\, dn_j$$

On integrating,

$$(G)_{T,\,p} = n_1\mu_1 + n_2\mu_2 + \ldots + n_j\mu_j = \Sigma n_i\mu_i \tag{7.20}$$

7.8 GIBBS-DUHEM EQUATION

At constant temperature and pressure, for a system of definite composition,

$$n_1 d\mu_1 + n_2 d\mu_2 + \ldots + n_j d\mu_j = 0$$

or

$$\sum_{i=1}^{j} n_i d\mu_i = 0$$

For example, for a binary system (two components)

$$n_1 d\mu_1 + n_2 d\mu_2 = 0$$

or

$$d\mu_1 = -\frac{n_2}{n_1}\, d\mu_2 \tag{7.21}$$

This means that chemical potentials for components 1 and 2 cannot be varied independently.

7.9 DEPENDENCE OF CHEMICAL POTENTIAL ON TEMPERATURE AND PRESSURE

(i) The variation of chemical potential (μ_i) of any constituent 'i' with temperature, at constant pressure and composition, is equal to the partial molar entropy of that constituent,

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,\,n_j} = -\bar{S_i} \tag{7.22}$$

(ii) The variation of chemical potential (μ_i) with pressure, at constant temperature and composition, is equal to the partial molar volume of that constituent,

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,\,n_j} = \bar{V}_i \tag{7.23}$$

7.10 CHEMICAL POTENTIAL FOR A COMPONENT IN AN IDEAL GAS MIXTURE

The chemical potential of any component of a mixture of ideal gases is determined by its partial pressure in the mixture as

$$\mu_i\,(p_i) = \mu_i^\circ + RT \ln p_i \tag{7.24}$$

where μ_i° is the chemical potential of the 'i'th component at temperature T when its partial pressure is p_i, and μ_i° is standard chemical potential (at one atmosphere pressure).

In terms of concentration C_i or mole fraction x_i

$$\mu_i\,(C_i) = \mu_i^\circ\,(C = 1) + RT \ln C_i$$

and
$$\mu_i\,(x_i) = \mu_i^{\circ\prime}\,(x = 1) + RT \ln x_i \tag{7.25}$$

where $\mu_i^\circ\,(C = 1)$ and $\mu_i^{\circ\prime}\,(x = 1)$ are the standard chemical potentials corresponding to unit concentration and mole fraction, respectively.

7.11 CONCEPT OF FUGACITY

To retain the form of free energy equations of ideal gases, for non-ideal gases, G.N. Lewis introduced two new terms *fugacity* and *activity*.

Fugacity is a kind of fictitious pressure used in order to retain, for real gases, simple forms of equations which are applicable to ideal gases only. Mathematically, fugacity 'f' is expressed as

$$\lim_{p \to 0} \frac{f}{p} \to 1 \tag{7.26}$$

i.e., as the pressure approaches zero fugacity approaches pressure. This means that fugacity is the measure of pressure of real gases.

For example, free energy may be expressed as

$$G = G^\circ + nRT \ln f$$

Change in free energy when fugacity changes from f_1 to f_2,

$$\Delta G = nRT \ln \frac{f_2}{f_1} \tag{7.27}$$

For one mole of gas, free energy may be written as

$$G_m = G_m^\circ + RT \ln f$$

But molar free energy is its chemical potential, so that

$$\mu = \mu^\circ + RT \ln f \tag{7.28}$$

where μ° is the standard chemical potential, i.e. chemical potential when fugacity is unity. For ideal gases fugacity is equal to pressure.

7.12 DETERMINATION OF FUGACITY OF REAL GASES

The fugacity for real gases may be expressed as

$$\ln \frac{f}{p} = \frac{1}{nRT}\int_0^p \left(V - \frac{nRT}{p} \right) dp$$

$$= \frac{1}{nRT}\int_0^p \alpha \, dp \tag{7.29}$$

The function $\left(V - \frac{nRT}{p}\right)$ is denoted by α and can be calculated from the equation of state data. The integral $\int_0^p \alpha \, dp$ is evaluated graphically (or numerically) up to any value of p and is equal to the area under the curve (α versus p). It may be noted that the area under the curve can be positive or negative, and hence fugacity may be greater or less than p.

7.13 CHANGE OF FUGACITY WITH PRESSURE AND TEMPERATURE

The dependence of fugacity on pressure, at constant temperature, may be expressed as

$$\left(\frac{\partial \ln f}{\partial p} \right)_T = \frac{\overline{V}}{RT} \tag{7.30}$$

In order to calculate fugacity at one pressure from the value at another, the equation may be integrated as

$$\ln \frac{f_2}{f_1} = \frac{1}{RT}\int_{p_1}^{p_2} \overline{V} \, dp$$

The change of fugacity with temperature is given by

$$\left(\frac{\partial \ln f}{\partial T} \right)_p = \frac{\overline{H}{*} - \overline{H}}{RT^2} \tag{7.31}$$

where H^* is the partial molar enthalpy of the given substance in state A^*, i.e. at zero pressure. Therefore, the difference $(H^* - H)$ is the change in molar enthalpy when the substance is transformed from state A to state A^* (state of zero pressure). The difference is also sometimes called the ideal heat of vaporization from state A.

7.14 CONCEPT OF ACTIVITY

In a standard state, the fugacity of a component is denoted by f° and its chemical potential as μ°. The difference in chemical potential between any state, in which chemical potential is μ, and standard state is given by the relation

$$\mu - \mu^\circ = RT \ln \frac{f}{f^\circ}$$

$$\mu = \mu^\circ + RT \ln \frac{f}{f^\circ} \tag{7.32}$$

The relative fugacity, f/f° (ratio of fugacities in the given state and the standard state), is called *activity* and is denoted by a.

$$\mu = \mu^\circ + RT \ln a \tag{7.33}$$

In the standard state, activity is unity, $a = 1\ (f^\circ / f^\circ)$ and $\mu = \mu^\circ$.

7.15 CHOICE OF STANDARD STATE

The standard state for a gas at any temperature is that in which the fugacity of the gas is equal to one, i.e. $f^\circ = 1$.

Since $a = \dfrac{f}{f^\circ}$ and $f^\circ = 1$, $\quad a = f$ (7.34)

Thus activity becomes numerically equal to fugacity for any gas. For ideal gases, fugacity is equal to the pressure. On the other hand, for real gases, fugacity and pressure are related through the activity coefficient (γ) as

$$f / p = \gamma \tag{7.35}$$

For solids and liquids there are several choices for the standard state. However, the one commonly used is the state of the pure solid or liquid at a pressure of 1 atm and the given temperature.

EXAMPLE 7.10 The Gibbs free energy of a water–alcohol system changes by 20 cal, at the given temperature and pressure, when 1.8 g of water is introduced into a large amount of the solution. What is the chemical potential of water?

Solution The chemical potential

$$\mu = \left(\frac{\partial G}{\partial n_i}\right)$$

$$dG = 20 \text{ cal}, \qquad dn_i = \frac{1.8}{18} = 0.1 \text{ mol}$$

$$\therefore \qquad \mu\,(H_2O) = \frac{20}{0.1} = 200 \text{ cal mol}^{-1}$$

EXAMPLE 7.11 Calculate $\mu - \mu^\circ$ for one mole of an ideal gas at 25°C and 600 torr pressure.

Solution $\mu = \mu^\circ + RT \ln (p \text{ atm})/(1 \text{ atm})$

or $\quad \mu - \mu^\circ = RT \ln (p \text{ atm})/(1 \text{ atm})$

$$R = 8.314 \text{ J mol}^{-1}\text{K}^{-1}, \qquad T = 25 + 273 = 298 \text{ K},$$

$$p = \frac{600}{760} \text{ atm}$$

$$\therefore \quad \mu - \mu^\circ = (8\ 314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (298\ \text{K}) \times 2.303 \log \frac{600}{760}$$

$$= -585.8\ \text{J}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 7.12 Calculate the free energy change for the following process :

1 mol H_2O (1, 100°C) ⟶ 1 mol H_2O (g, 100°C)

Solution For the process,

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta H = \Delta H_{\text{evap}}$$

and
$$\Delta S = \frac{\Delta H_{\text{evap}}}{T_b}$$

$$\therefore \quad \Delta G = \Delta H_{\text{evap}} - T_b \left(\frac{\Delta H_{\text{evap}}}{T_b}\right) \qquad (T = T_b)$$

$$= 0$$

$\Delta G = 0$ because the phase change is an equilibrium process at the phase transition temperature and pressure.

EXAMPLE 7.13 The e.m.f. of the cell reaction

$$\text{Zn(s)} + 2\text{Ag}^+\text{(aq)} \longrightarrow \text{Zn}^{2+}\text{(aq)} + 2\text{Ag(s)}$$

is 1.56 V at 25°C. Calculate ΔG° and predict whether the reaction will occur spontaneously from left to right or not.

Solution The change in free energy is related to the electrical work as

$$\Delta G^\circ = -\ nF\ E^\circ$$

where n is the number of moles of electrons, F is the Faraday of electricity, and E° is the standard cell potential.

$$n = 2, \qquad F = 9.65 \times 10^4\ \text{J mol}^{-1}\text{V}^{-1}, \qquad E^\circ = 1.56\ \text{V}$$

$$\Delta G^\circ = -\ (2\ \text{mol}) \times (9.65 \times 10^4\ \text{J mol}^{-1}\text{V}^{-1}) \times (1.56\ \text{V})$$

$$= -\ 301.08\ \text{kJ}$$

Since ΔG° for the reaction is negative, it will be spontaneous from left to right.

EXAMPLE 7.14 Calculate the Gibbs free energy change and the enthalpy change for the process:

1 mol benzene (l, 80.1°C, 1 atm) ⟶ 1 mol benzene (g, 80.1°C, 0.5 atm)

The normal boiling point of benzene is 80.1°C and the enthalpy of vaporization is 395 J g^{-1}. Consider benzene vapours as ideal gas.

Solution ΔH and ΔG can be calculated by the following reversible path:

(i) 1 mol C_6H_6 (l, 80.1°C, 1 atm) ⟶ 1 mol C_6H_6 (g, 80.1°C, 1 atm)

$$\Delta H_1 = (395\ \text{J g}^{-1}) \times (78\ \text{g mol}^{-1}) = 30.810\ \text{kJ mol}^{-1}$$

$\Delta G_1 = 0$ (phase change is an equilibrium process).

(ii) C_6H_6 (g, 80.1°C, 1 atm) $\longrightarrow$ C_6H_6 (g, 80.1°C, 0.5 atm)

$$\Delta H_2 = 0$$

$$\Delta G_2 = nRT \ln \frac{p_2}{p_1}$$

$n = 1$ mol, $R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}$, $T = 273+80.1 = 353.1$ K,
$p_1 = 1$ atm, $p_2 = 0.5$ atm

$$\Delta G_2 = 1 \times 8.314 \times 353.1 \times 2.303 \log \frac{0.5}{1}$$
$$= -\ 2.035\ \text{kJ mol}^{-1}$$

Thus, total $\Delta H = 30.810 + 0 = 30.810\ \text{kJ mol}^{-1}$
$\Delta G = 0 + (-\ 2.035) = -\ 2.035\ \text{kJ mol}^{-1}$

EXAMPLE 7.15 Calculate the Gibbs free energy change when the partial pressure of one mole of N_2 is decreased from 10 atm to 5 atm at 27°C.

Solution Free energy change can be calculated from the difference of chemical potential when the pressures are 5 atm and 10 atm. The chemical potential of N_2 can be calculated as:

$$\mu = \mu^\circ + RT \ln p_i$$

or

$$\mu - \mu^\circ = RT \ln p_i$$

(i) When $p_i = 5$ atm, $T = 27 + 273 = 300$ K

$$\mu - \mu^\circ = (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (300\ \text{K}) \times 2.303 \log 5$$
$$= 4.015\ \text{kJ}$$

(ii) When $p_i = 10$ atm, $T = 300$ K

$$\mu' - \mu^\circ = (8.314\ \text{J K}^{-1}\text{mol}^{-1}) \times (300\ \text{K}) \times 2.303 \log 10$$
$$= 5.744$$

Change in free energy when 1 mole of N_2 is transferred from 10 atm to 5 atm,

$$\Delta G = (1\ \text{mol}) \times (\mu - \mu')$$
$$= (1\ \text{mol}) \times [(\mu - \mu^\circ) - (\mu' - \mu^\circ)]$$
$$= (1\ \text{mol}) \times [4.015 - 5.744] = -\ 1.729\ \text{kJ}$$

Alternatively, it may be calculated as,

$$\Delta G = nRT \ln \frac{p_2}{p_1} = (1\ \text{mol}) \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (300\ \text{K}) \times \left(2.303 \log \frac{5}{10}\right)$$
$$= -1.729\ \text{kJ}$$

QUESTIONS

Numerical Problems

7.1 Calculate the standard Gibbs free energy change for the combustion of methane:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

at 25°C; $\Delta H^\circ = -\ 191.8$ kcal and $\Delta S^\circ = 1.2\ \text{cal K}^{-1}$

7.2 ΔH and ΔS for a reaction at 27°C are $-$ 10 kcal and 20 cal K^{-1}, respectively. What is ΔG for the reaction ? Predict whether the reaction will be feasible or not ?

7.3 (SI Units) Calculate the value of $(\Delta G - \Delta A)$ for the following reactions at 300 K:

(a) $C_6H_5COOH(s) + \frac{13}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$

(b) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$

(c) $C_6H_6(l) + \frac{15}{2}O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(g)$

7.4 The standard e.m.f. of cells at 25°C are given:

(a) $Zn \mid Zn^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu$; $E° = 1.10$ V

(b) $Pt \mid H_2(1\ atm), H^+(1M) \parallel Zn^{2+}(1M) \mid Zn$; $E° = -0.763$ V

Calculate $\Delta G°$ for the cell reactions and predict which of these is spontaneous.

7.5 (SI Units) The standard free energy of formation of $C_6H_6(l)$ and $C_2H_2(g)$ are 172.80 and 209.20 kJ mol^{-1}, respectively. Calculate $\Delta G°$ for the conversion of acetylene to benzene.

7.6 $\Delta G°$ for the reaction

$$C_2H_5OH(l) + 3O_2(g) \longrightarrow 2\ CO_2(g) + 3H_2O(l)$$

at 298 K is $-$ 1326.2 kJ mol^{-1}. Calculate the free energy of formation of ethanol given that $\Delta G_f°$ for $CO_2 = -$ 394.4 kJ mol^{-1},

$\Delta G_f°$ for $H_2O(l) = -$ 237.2 kJ mol^{-1} at 298 K.

7.7 Urea can be synthesized according to the reaction

$$2NH_3(g) + CO_2(g) \longrightarrow NH_2CONH_2(s) + H_2O(l)$$

Calculate $\Delta G°$ for the reaction at 298 K given that

$\Delta G_f°\ (NH_2CONH_2) = -$ 197.2 kJ mol^{-1}, $\Delta G_f°\ (CO_2) = -$ 394.4 kJ mol^{-1},

$\Delta G_f°\ (H_2O) = -$ 273.2 kJ mol^{-1}, $\Delta G_f°\ (NH_3) = -$ 16.6 kJ mol^{-1}.

7.8 (SI Units) For the reaction,

$$N_i(s) + Cl_2(g) \longrightarrow N_iCl_2(s)$$

$\Delta H° = -$ 305 kJ mol^{-1} at 298 K and the entropies of various substances at 298 K are

$S°(Ni) = 30.1$ J K^{-1} mol^{-1}, $S°(Cl_2) = 223.3$ J K^{-1} mol^{-1}

$S°(NiCl_2) = 97.4$ J K^{-1} mol^{-1}.

Calculate $\Delta G°$ for the reaction.

7.9 ΔG for a reaction at 300 K and 310 K are $-$ 29.1 kcal mol^{-1} and $-$ 25.8 kcal mol^{-1}, respectively. Calculate ΔH and ΔS for the reaction between this temperature range.

7.10 (SI Units) For the reaction

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

at 298 K, $\Delta H° = -$ 92.4 kJ, $\Delta S° = -$ 198.3 J. Calculate ΔG for the reaction at (i) 298 K (ii) 500 K.

7.11 The free energy change accompanying a given reaction is $-$ 22.8 kcal mol^{-1} at 25°C, and $-$ 21.6 kcal mol^{-1} at 35°C. Calculate the change in enthalpy for the reaction at 30°C.

7.12 Calculate the Gibbs free energy change when five moles of an ideal gas are compressed isothermally from 1 atm to 100 atm at 25°C.

7.13 (SI Units) Two moles of an ideal gas, initially at 300 K and 1.01×10^5 Nm^{-2} are compressed isothermally till the pressure becomes 6.06×10^5 Nm^{-2}. Calculate the Gibbs free energy change for the process.

7.14 Calculate ΔG for the isothermal expansion of one mole of an ideal gas at 27°C from a pressure of 760 torr to 76 torr.

7.15 (SI Units) Four moles of an ideal gas expand isothermally from 1 dm^3 to 10 dm^3, at 300 K. Calculate the change in the free energy of the gas.

7.16 Calculate the value of $\mu - \mu^\circ$ for two moles of an ideal gas at 127°C and 450 torr pressure.

7.17 The density of nitrogen at 0°C and 1 atm pressure is $1.25\ \text{g}\ l^{-1}$. Calculate the fugacities of nitrogen under these conditions.

7.18 Calculate ΔG° for the reaction:

$$H_2S(g) + \tfrac{3}{2}\,O_2(g) \longrightarrow SO_2(g) + H_2O(l)$$

from the following data

Substance	ΔH_f° (kJ mol^{-1})	S°(J K^{-1}mol^{-1})
$H_2S(g)$	− 20.1	205.6
$SO_2(g)$	− 296.1	248.5
$H_2O(l)$	− 285.8	69.9
$O_2(g)$	0	205.0

7.19 The Gibbs free energy of a water–ethanol system changes by 35 cal at a given temperature when 3.6 g of water is introduced into a large amount of solution. What is the chemical potential of water ?

7.20 The vapour pressure of ice at − 5°C is 3.012 torr and that of super-cooled liquid water is 3.163 torr. Calculate the molar free energy for the process:

Ice (− 5°C) ⟶ Water (super-cooled, − 5°C).

Quiz Questions

Type A: Multiple Choice

7.21 The Helmholtz free energy A of any system is defined as

(a) $A = U + TS$
(b) $A = U - TS$
(c) $A = U - pV$
(d) $A = H - TS$

7.22 At constant temperature, the decrease in Helmholtz free energy is equal to the

(a) reversible work done by the system
(b) decrease in entropy
(c) total work done minus pressure volume work in a reversible manner
(d) irreversible work done by the system

7.23 At constant p and T the change in Gibbs free energy (ΔG) may be expressed as

(a) $\Delta G = \Delta H - T\,\Delta S$
(b) $\Delta G = \Delta H + T\,\Delta S$
(c) $\Delta G = \Delta U - T\,\Delta S$
(d) $\Delta G = \Delta H - \Delta U + p\ \Delta V$

7.24 Which of the following does not express the criterion for the spontaneity ?

(a) $(dU)_{S,V,T} \leqslant 0$
(b) $(dS)_{U,V,T} \geqslant 0$
(c) $(dA)_{V,T} \geqslant 0$
(d) $(dG)_{p,T} \leqslant 0$

7.25 At constant p and T, the criterion of spontaneity is

(a) $dG \geqslant 0$
(b) $dA \leqslant 0$
(c) $dA \geqslant 0$
(d) $dG \leqslant 0$

7.26 The variation of Gibbs free energy change with temperature is expressed by

(a) $\dfrac{\partial(\Delta G/T)}{\partial T} = -\dfrac{\Delta S}{T^2}$

(b) $\dfrac{\partial(\Delta G)}{\partial T} = \dfrac{\Delta H}{T^2}$

(c) $\dfrac{\partial(\Delta G/T)}{\partial T} = -\dfrac{\Delta H}{T^2}$

(d) $\dfrac{\partial(\Delta G)}{\partial T} = -\dfrac{\Delta H}{T}$

7.27 Consider the thermodynamic equations,

$$dA = -pdV - SdT$$

and $$dG = Vdp - SdT$$

Which of the following is not correct ?

(a) $\left(\dfrac{\partial A}{\partial V}\right)_T = -p$

(b) $\left(\dfrac{\partial A}{\partial T}\right)_V = -p$

(c) $\left(\dfrac{\partial G}{\partial p}\right)_T = V$

(d) $\left(\dfrac{\partial G}{\partial T}\right)_p = -S$

7.28 For the expression $dG = Vdp - SdT$, which of the following is correct ?

(a) $\left(\dfrac{\partial G}{\partial p}\right)_T = -S$

(b) $\left(\dfrac{\partial G}{\partial T}\right)_p = V$

(c) $\left(\dfrac{\partial G}{\partial T}\right)_S = V$

(d) $\left(\dfrac{\partial G}{\partial p}\right)_T = V$

7.29 The relation of Helmholtz free energy change with temperature $\partial(\Delta A/T)/\partial T$ is equal to

(a) $-\dfrac{\Delta U}{T}$

(b) $\dfrac{\Delta U}{T^2}$

(c) $-\dfrac{\Delta U}{T^2}$

(d) $T\,\Delta U$

7.30 If n_1 and n_2 represent moles of two components and μ_1 and μ_2 their chemical potentials, respectively, then the Gibbs Duhem equation for this binary system is written as

(a) $n_1\,d\mu_2 + n_2 d\mu_1 = 0$

(b) $n_1 d\mu_1 + n_2 d\mu_2 > 0$

(c) $n_1 d\mu_1 + n_2 d\mu_2 = 0$

(d) $n_1 d\mu_1 - n_2 d\mu_2 = 0$

7.31 The term chemical potential was first introduced by

(a) Gibbs

(b) Duhem

(c) Einstein

(d) Maxwell

7.32 The variation of chemical potential with pressure may be expressed as

(a) $\left(\dfrac{\partial \mu_1}{\partial p}\right)_{T,n_j} = \overline{S_i}$

(b) $\left(\dfrac{\partial \mu_1}{\partial p}\right)_{T,n_j} = \overline{V_i}$

(c) $\left(\dfrac{\partial \mu_1}{\partial p}\right)_{T,n_j} = \overline{G_i}$

(d) $\left(\dfrac{\partial \mu_1}{\partial p}\right)_{T,n_j} = -\overline{S_i}$

7.33 The change of chemical potential of any component, with temperature, at constant pressure and composition, is equal to the
(a) partial molar volume
(b) negative of the partial molar entropy
(c) partial molar free energy
(d) partial molar enthalpy of that constituent

7.34 The chemical potential of a component (having partial pressure p_i) of a mixture of ideal gases is expressed as
(a) $\mu_i = \mu_i^\circ(p) - RT \ln p_i$
(b) $\mu_i = \mu_i^\circ(p) + \dfrac{\ln p_i}{RT}$
(c) $\mu_i = \mu_i^\circ(p) + RT \ln p_i$
(d) $\dfrac{\mu_i}{\mu_i^\circ(p)} = RT \ln p_i$

7.35 A kind of fictitious pressure used in order to retain, for real gases, simple forms of equations which are applicable to ideal gases, is called
(a) non-ideal pressure
(b) activity
(c) fugacity
(d) escaping pressure

7.36 Activity is defined as
(a) concentration in the standard state
(b) ratio of the fugacities in the given and standard states
(c) concentration of the solute when its chemical potential is zero
(d) ratio between the actual pressure and the pressure in the ideal gas, at the same concentration

7.37 In a solution, the activity of the solvent is
(a) always less than unity
(b) always more than unity
(c) equal to unity
(d) equal to fugacity

7.38 During a solid–liquid transition at melting point,
(a) $\Delta U = 0$
(b) $\Delta H = 0$
(c) $\Delta S = 0$
(d) $\Delta G = 0$

7.39 The correct expression for the chemical potential of a component '*i*' in the mixture is
(a) $\left(\dfrac{\partial G}{\partial n_i}\right)_{T,\,p,\,n_j}$
(b) $\left(\dfrac{\partial U}{\partial n_i}\right)_{S,\,p,\,n_j}$
(c) $\left(\dfrac{\partial H}{\partial n_i}\right)_{S,\,V,\,n_j}$
(d) $\left(\dfrac{\partial A}{\partial n_i}\right)_{T,\,p,\,n_j}$

7.40 The relationship between the Gibbs free energy (G) and Helmholtz free energy (A) is
(a) $G = A - TS$
(b) $G = A + H - pV$

(c) $G = A + pV$
(d) $A = G - TS$

7.41 The Gibbs-Helmholtz equation may be expressed in one of the following forms

(a) $\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_p$
(b) $\left[\frac{\partial \Delta G}{\partial T}\right]_p = -\frac{\Delta H}{RT^2}$
(c) $\left[\frac{\partial(\Delta G/T)}{\partial T}\right]_p = \frac{\Delta H}{RT^2}$
(d) $\Delta G = \frac{\Delta H}{T^2} - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$

7.42 Which of the following relations is incorrect ?

(a) $\left(\frac{\partial G}{\partial T}\right)_p = -S$
(b) $\left(\frac{\partial G}{\partial p}\right)_T = V$
(c) $\frac{\partial(A/T)}{\partial T} = -\frac{U}{T^2}$
(d) $\frac{\partial(G/T)}{\partial T} = -\frac{H}{T}$

7.43 If $(dG)_{p,\,T} < 0$, the process
(a) does not occur
(b) is feasible
(c) has ceased to occur
(d) can occur only at high pressures

7.44 In the standard state for a gas, at any given temperature,
(a) activity = 1
(b) fugacity = 1
(c) activity > fugacity
(d) fugacity = 0

7.45 The free energy change in an isothermal compression of n moles of an ideal gas, when pressure changes from p_1 to p_2 may be expressed as

(a) $\Delta G = nRT \ln \frac{p_1}{p_2}$
(b) $\Delta G = \int_{p_1}^{p_2} \frac{n}{RT} p \, dp$
(c) $\Delta G = V(p_2 - p_1)$
(d) $\Delta G = nRT \ln \frac{p_2}{p_1}$

TYPE B: Multiple Choice (Numericals)

7.46 The Gibbs free energy of a reaction at 300 K and 310 K are −29 kcal and −29.5 kcal, respectively. ΔS for the reaction in this temperature range is
(a) 58.5 cal deg^{-1}
(b) −50 cal deg^{-1}
(c) 50 cal deg^{-1}
(d) −58.5 cal deg^{-1}

7.47 ΔG for a reaction at 300 K is -16 kcal and ΔH is -10 kcal. The entropy of the reaction is

(a) 20 cal deg^{-1}
(b) 86.6 cal deg^{-1}
(c) 166 cal deg^{-1}
(d) 100 cal deg^{-1}

7.48 The activity coefficient of a gas at $p = 4$ atm is 1.04. Its fugacity is

(a) 4.16 (b) 0.26
(c) 0.74 (d) 3.8

7.49 The fugacity of a pure liquid substance at 25°C is 90 torr. In a solution at the same temperature, its mole fraction is 0.25 and fugacity is 18 torr. The activity coefficient of the substance in the solution is

(a) 0.20 (b) 0.50
(c) 0.75 (d) 0.80

7.50 The activity coefficient of a gas in a gaseous mixture is 0.3. The fugacity of the gas in its standard state is 90 torr. The fugacity of the gas in the mixture is

(a) 30 torr (b) 0.0003 torr
(c) 27 torr (d) 2.7 torr

7.51 Calculate the free energy change accompanying the compression of 1 mol of a gas at 27°C from 20 to 200 atmospheres (R=2 cal K^{-1} mol^{-1})

(a) 138.18 cal (b) 13818 cal
(c) 1381.8 cal (d) -1381.8 cal

7.52 The Gibbs free energy of a reaction at 27°C is -26 kcal and its entropy change is 60 cal/deg. ΔH of the reaction is

(a) -44 kcal (b) -8 kcal
(c) 34 kcal (d) -14 kcal

7.53 One mole of an ideal gas expands reversibly and isothermally, at 27°C, from the initial volume of 5 *l* to 50 *l*. ΔG for the reaction is (R=2 cal K^{-1} mol^{-1})

(a) 1.382 kcal (b) —1.382 kcal
(c) 1382.8 kcal (d) -1381.8 kcal

7.54 A liquid freezes into a solid at 200 K and 1 atm. ΔH of the reaction is -1200 cal mol^{-1}. The freezing will be spontaneous at (assume ΔH and ΔS remain constant)

(a) 205 (b) 210 K
(c) 195 (d) 201

7.55 For the reaction

$$A + 2B \longrightarrow C + D$$

$$\Delta H = -25 \text{ kcal and}$$

$$\Delta S = 90 \text{ cal deg}^{-1} \text{ at } 27°\text{C}.$$

The reaction

(a) is irreversible at 27°C
(b) is not feasible at 27°C
(c) represents equilibrium state at 27°C
(d) can occur only at temperatures higher than 27°C

TYPE C: True or False

7.56 The decrease in Helmholtz free energy is equal to the amount of reversible work done.

7.57 At constant pressure and temperature, the criterion of spontaneity is $dG \leqslant 0$.

7.58 Chemical potential is an extensive property.

7.59 The variation of chemical potential with pressure, at constant temperature and composition, is equal to the partial molar entropy.

7.60 The ratio of fugacities in the given state to those in the standard state is called the activity coefficient.

7.61 The activity of a solvent in a solution is always less than unity.

7.62 In case of gases, the standard state at any temperature is that in which the fugacity of the gas is equal to zero.

7.63 The Gibbs free energies of elements in their most stable forms are arbitrarily fixed as equal to zero at 1 atm pressure and 0°C.

7.64 The chemical potential of a constituent of a mixture is its contribution per mole to the total free energy of the system of a constant composition at constant temperature and pressure.

7.65 In a solution, the fugacity of the solvent will always be less than that of the pure solvent at the same temperature and pressure.

TYPE D: Fill in the Blanks

7.66 If a process, under constant conditions of temperature and pressure, is accompanied by a decrease of free energy, the process is ————.

7.67 At equilibrium, free energy change is ————.

7.68 The partial molar quantities are concerned with ———— properties.

7.69 For an ideal gas mixture, the fugacity of a gas is equal to its ————.

7.70 The fictitious pressure used in order to retain simple forms of equations of ———— gases for ———— gases is called ————.

ANSWERS

Numerical Problems

7.1 −192.2 kcal *7.2* −16 kcal, feasible *7.3* (a) −1247.1 J (b) −2494.2 J (c) −3741.3 J *7.4* (a) −212.3 kJ (b) 147.3 kJ (c) is feasible *7.5* −454.8 kJ *7.6* −174.2 kJ *7.7* −6.8 kJ mol^{-1} *7.8* −258.5 *7.9* −128.1 *7.10* (i) −33.31 (ii) 26.37 *7.11* −46.44 *7.12* 13.589 *7.13* 8.94 *7.14* −1.368 *7.15* 22.98 *7.16* −520.0 J *7.17* (a) 1.001 atm, (b) 98.14 atm *7.18* −503.8 *7.19* 175 *7.20* −109 J mol^{-1}

Quiz Questions

7.21 (b) *7.22* (a) *7.23* (a) *7.24* (c) *7.25* (d) *7.26* (c) *7.27* (b) *7.28* (d) *7.29* (c) *7.30* (c) *7.31* (a) *7.32* (b) *7.33* (b) *7.34* (c) *7.35* (c) *7.36* (b) *7.37* (a) *7.38* (d) *7.39* (a) *7.40* (a) *7.41* (a) *7.42* (d) *7.43* (b) *7.44* (b) *7.45* (d) *7.46* (c) *7.47* (a) *7.48* (a) *7.49* (d) *7.50* (c) *7.51* (c) *7.52* (a) *7.53* (b) *7.54* (c) *7.55* (b) *7.56* True *7.57* True *7.58* False *7.59* False: it is equal to partial molar volume *7.60* False: it is called activity *7.61* True *7.62* False *7.63* False *7.64* True *7.65* False *7.66* irreversible *7.67* zero *7.68* extensive *7.69* partial pressure *7.70* ideal, real, fugacity.

8

Chemical Equilibrium

It is a common observation that many reactions do not go to completion. The amounts of reactants left depend on the experimental conditions (temperature, pressure, etc.) and the nature of the reaction. The question as to how far a reaction proceeds is very important in chemistry and chemical engineering.

8.1 EQUILIBRIUM STATE

The state in which the measurable properties of a system (such as pressure, density, colour or concentration of species) do not undergo any noticeable change with time, under a given set of conditions, is said to be a state of equilibrium.

Characteristics of Chemical Equilibrium

The important characteristics of chemical equilibrium are:

(1) The properties of the system become constant at equilibrium and remain unchanged thereafter.

(2) The equilibrium can be approached from either direction, i.e. starting with pure reactants or pure products, provided enough time is allowed.

(3) The chemical equilibrium is dynamic in nature. It may be noted that, after the attainment of equilibrium, the reaction does not stop. In fact, both the forward and backward reactions continue at equilibrium but the rates of the two opposing reactions become equal.

(4) A catalyst can hasten the approach towards equilibrium but it does not change the state of equilibrium.

8.2 LAW OF CHEMICAL EQUILIBRIUM

Consider a simple reversible reaction,

$$A + B \rightleftharpoons C + D$$

According to the law of mass action,
Rate of forward reaction, $R_f = k_f\, a_A \times a_B$
Rate of reverse reaction, $R_r = k_r\, a_C \times a_D$
where a_A, a_B, a_C and a_D are the activities of the substances A, B, C and D, respectively. k_f and k_r are the rate constants for the forward and the backward reaction, respectively.

At equilibrium, the rates of forward and reverse reactions become equal, $R_f = R_r$, so that

$$k_f\, a_A \times a_B = k_r\, a_C \times a_D$$

or

$$K = \frac{k_f}{k_r} = \frac{a_C \times a_D}{a_A \times a_B} \tag{8.1}$$

where K is called the *thermodynamic equilibrium constant*. In some cases (low concentration or pressure), it is convenient to replace activities by concentrations and we have

$$K_c = \frac{C_C \times C_D}{C_A \times C_B} \tag{8.2}$$

For a general reaction,

$$aA + bB + \ldots \rightarrow lL + mM + \ldots$$

$$K_c = \frac{C_L^l \times C_M^m \times \ldots}{C_A^a \times C_B^b \times \ldots} \tag{8.3}$$

The concentrations of species A, B, etc. are also written as [A], [B], etc. so that

$$K_c = \frac{[L]^l\,[M]^m \ldots}{[A]^a\,[B]^b \ldots}$$

8.3 DIFFERENT FORMS OF EQUILIBRIUM CONSTANTS

Equation (8.3) expresses the equilibrium constant in terms of concentrations (mol l^{-1} or mol dm^{-3}). For gaseous reactions, the concentrations are related to pressure through the gas equation, $C = \dfrac{n}{V} = \dfrac{p}{RT}$ and Equation (8.3) becomes

$$K_c = \frac{\left(\dfrac{p_L}{RT}\right)^l \times \left(\dfrac{p_M}{RT}\right)^m \cdots}{\left(\dfrac{p_A}{RT}\right)^a \times \left(\dfrac{p_B}{RT}\right)^b \cdots}$$

$$= \frac{p_L^l \times p_M^m \cdots}{p_A^a \times p_B^b \cdots} \times \left(\frac{1}{RT}\right)^{(l+m+\cdots)-(a+b+\cdots)}$$

The quantity $$\frac{p_{\text{L}}^{l} \times p_{\text{M}}^{m} \times \ldots}{p_{\text{A}}^{a} \times p_{\text{B}}^{b} \times \ldots} \tag{8.4}$$

is defined as K_p and is constant at a given temperature. Thus, K_p and K_c are related as

$$K_c = K_p \times \left(\frac{1}{RT}\right)^{\Delta n} \tag{8.5}$$

or $$K_p = K_c \times (RT)^{\Delta n} \tag{8.6}$$

where $\Delta n = (l + m + \ldots) - (a + b + \ldots)$ is the difference between the number of gaseous moles of the products and reactants in the chemical equation for the reaction.

The concentrations can also be expressed in terms of mole fractions (x) and therefore, for a general reaction

$$a\text{A} + b\text{B} + \ldots = l\text{L} + m\text{M} \ldots$$

$$K_x = \frac{x_{\text{L}}^{l} \times x_{\text{M}}^{m} \times \ldots}{x_{\text{A}}^{a} \times x_{\text{B}}^{b} \times \ldots} \tag{8.7}$$

Now, partial pressure p_{A} is related to total pressure p as $p_{\text{A}} = x_{\text{A}}p$, etc. Thus, equation (8.4) becomes,

$$\begin{aligned} K_p &= \frac{(x_{\text{L}}p)^{l} \times (x_{\text{M}}p)^{m} \ldots}{(x_{\text{A}}p)^{a} \times (x_{\text{B}}p)^{b} \ldots} \\ &= \frac{(x_{\text{L}})^{l} \times (x_{\text{M}})^{m} \ldots}{(x_{\text{A}})^{a} \times (x_{\text{B}})^{b} \ldots} \times p^{(l + m + \cdots) - (a + b + \cdots)} \end{aligned}$$

or $$K_p = K_x p^{\Delta n} \tag{8.8}$$

From Equations (8.6) and (8.8) we get

$$K_c \times (RT)^{\Delta n} = K_x\, p^{\Delta n} \quad \text{or } K_c = K_x \left(\frac{p}{RT}\right)^{\Delta n} \tag{8.9}$$

Example 8.1 What will be the equilibrium concentrations of H_2, I_2 and HI if, initially, 5 millimoles of H_2 and 2 millimoles of I_2 are introduced in a one-litre flask thermostated at 27°C? (K_c for the reaction is 16.34 at 27°C).

Solution According to the reaction,

$$H_2 + I_2 \rightleftharpoons 2HI$$

One mole of H_2 reacts with one mole of I_2 to form two moles of HI. Let us suppose that x millimoles of H_2 react with x millimoles of I_2 to give $2x$ millimoles of HI and equilibrium is established.

Then at equilibrium,

$$\begin{aligned} H_2 &= (5 - x) \times 10^{-3} \text{ mol } l^{-1} \\ I_2 &= (2 - x) \times 10^{-3} \text{ mol } l^{-1} \\ HI &= 2x \times 10^{-3} \text{ mol } l^{-1} \end{aligned}$$

$$K_c = \frac{[\text{HI}]^2}{[H_2][I_2]} = \frac{(2x \times 10^{-3})^2}{(5 - x) \times 10^{-3} \times (2 - x) \times 10^{-3}}$$

or $$12.34x^2 - 114.38x + 163.4 = 0$$

Solving the quadratic equation, we get $x = 1.77$ millimoles. Thus, equilibrium concentrations are:

$$[H_2] = 5 - 1.77 = 3.23 \text{ millimoles/litre}$$
$$[I_2] = 2 - 1.77 = 0.23 \text{ millimoles/litre}$$
$$[HI] = 2 \times 1.77 = 3.54 \text{ millimoles/litre}$$

EXAMPLE 8.2 (SI Units) During the preparation of carbon monoxide by the reaction:

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

at 1175K and 1.02×10^5 N m^{-2} pressure, the partial pressures of CO_2, H_2 and CO are 2.18×10^4, 2.58×10^4 and 2.72×10^4 N m^{-2}, respectively,

(a) Calculate K_p for the reaction.

(b) What will be K_p for the reaction,

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

at the same temperature?

Solution (a) For the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

$$K_p = \frac{p_{(CO)} \times p_{(H_2O)}}{p_{(CO_2)} \times p_{(H_2)}}$$

$$p_{(CO_2)} = 2.18 \times 10^4 \text{ N m}^{-2}, \quad p_{(H_2)} = 2.58 \times 10^4 \text{ N m}^{-2},$$

$$p_{(CO)} = 2.72 \times 10^4 \text{ N m}^{-2}$$

$$\begin{aligned} p_{(H_2O)} &= p - [p_{(CO)} + p_{(H_2)} + p_{(CO_2)}] \\ &= 1.02 \times 10^5 - [2.72 + 2.58 + 2.18] \times 10^4 \\ &= 2.72 \times 10^4 \text{ N m}^{-2} \end{aligned}$$

$$\therefore \quad K_p = \frac{(2.72 \times 10^4 \text{ N m}^{-2}) \times (2.72 \times 10^4 \text{ N m}^{-2})}{(2.18 \times 10^4 \text{ N m}^{-2}) \times (2.58 \times 10^4 \text{ N m}^{-2})} = 1.32$$

(b) The equilibrium constant K'_p for the reverse reaction is related to the equilibrium constant for the forward reaction K_p as

$$K'_p = \frac{1}{K_p} = \frac{1}{1.32} = 0.76$$

EXAMPLE 8.3 In an experiment at 1000 K the concentrations of NH_3, H_2 and N_2 at equilibrium are

$$[NH_3] = 0.105 \text{ mol dm}^{-3}, \quad [N_2] = 1.10 \text{ mol dm}^{-3} \text{ and}$$
$$[H_2] = 1.50 \text{ mol dm}^{-3}$$

Calculate the values of K_c and K_p for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Solution For the reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3}$$

$$[NH_3] = 0.105 \text{ mol dm}^{-3}, \quad [N_2] = 1.10 \text{ mol dm}^{-3},$$
$$[H_2] = 1.50 \text{ mol dm}^{-3}$$

$$K_c = \frac{(0.105 \text{ mol dm}^{-3})^2}{(1.10 \text{ mol dm}^{-3}) \times (1.50 \text{ mol dm}^{-3})^3}$$

$$= 2.97 \times 10^{-3} \text{ mol}^{-2} \text{ dm}^6$$

Now, $K_p = K_c\,(RT)^{\Delta n}$

$\Delta n = 2 - (3 + 1) = -2, \quad R = 0.082 \text{ atm dm}^3 \text{ K}^{-1}\text{mol}^{-1},$

$T = 1000 \text{ K}$

$$K_p = (2.97 \times 10^{-3}\text{mol}^{-2}\text{dm}^6) \times [(0.082 \text{ atm dm}^3 \text{ K}^{-1}\text{mol}^{-1}) \times (1000 \text{ K})]^{-2}$$

$$= 4.42 \times 10^{-7} \text{ atm}^{-2}$$

EXAMPLE 8.4 (a) Determine the equilibrium constant K_p for the reaction

$$CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$

if the partial pressures in a vessel at 3000 K and at equilibrium are

$$p_{(CO)} = 0.4 \text{ atm}, \quad p_{(CO_2)} = 0.6 \text{ atm and } p_{(O_2)} = 0.2 \text{ atm}$$

(b) Calculate K_c and K_x for the above reaction.

Solution For the reaction,

$$CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$

$$K_p = \frac{p_{(CO_2)}}{p_{(CO)} \times p_{(O_2)}^{\;1/2}}$$

$p_{(CO_2)} = 0.6 \text{ atm}, \quad p_{(CO)} = 0.4 \text{ atm and } p_{(O_2)} = 0.2 \text{ atm}$

$$K_p = \frac{0.6 \text{ atm}}{(0.4 \text{ atm}) \times (0.2 \text{ atm})^{1/2}} = 3.354 \text{ atm}^{-1/2}$$

(b) K_p and K_c are related as

$K_c = K_p \times (RT)^{-\Delta n}$

$\Delta n = 1 - (1 + \tfrac{1}{2}) = -\tfrac{1}{2}, \; R = 0.082 \text{ atm } l \text{ K}^{-1}\text{mol}^{-1},$

$T = 3000 \text{ K}$

$K_c = (3.354 \text{ atm}^{-1/2}) \times [(0.082 \text{ atm } l \text{ K}^{-1}\text{mol}^{-1}) \times 3000 \text{ K}]^{1/2}$

$= 52.64 \text{ mol}^{-1/2}\, l^{1/2}$

K_x and K_p are related as

$K_x = K_p \times (p)^{-\Delta n}$

$\Delta n = -\tfrac{1}{2}$, Total pressure, $p = 0.4 + 0.6 + 0.2 = 1.2 \text{ atm}$

$K_x = 3.354 \text{ atm}^{-1/2} \times (1.2 \text{ atm})^{1/2}$

$= 3.67$

EXAMPLE 8.5 (SI Units) Calculate the ratio of K_p to K_c at 300 K for the following reactions:

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(c) $NH_4Cl(s) \rightleftharpoons HCl(g) + NH_3(g)$

Solution

(a) Ratio of K_p and K_c is

$K_p = K_c\,(RT)^{\Delta n}$

or $$\frac{K_p}{K_c} = (RT)^{\Delta n}$$

For the reaction (a) $\Delta n = 2 - (1 + 3) = -2$, $R = 0.082$ atm l K^{-1}mol^{-1}, $T = 300$ K

$$\frac{K_p}{K_c} = [(0.082 \text{ atm } l \text{ K}^{-1}\text{mol}^{-1}) \times (300 \text{ K})]^{-2}$$

$$= 1.65 \times 10^{-3} \text{ atm}^{-2}\, l^{-2}\text{mol}^2$$

(b) For the reaction $\Delta n = 2 - (1 + 1) = 0$

$$\frac{K_p}{K_c} = (\text{RT})^{\circ} = 1$$

(c) For the reaction $\Delta n = 1 + 1 - 0 = 2$

$$\frac{K_p}{K_c} = [(0.082 \text{ atm } l \text{ K}^{-1}\text{mol}^{-1}) \times (300 \text{ K})]^2$$

$$= 605.2 \text{ atm}^2\, l^2 \text{ mol}^{-2}$$

Note The units of the ratio of K_p to K_c depend upon the units of K_p and K_c for the reaction. For example, for reaction (a)

$$K_p = \frac{(\text{atm})^2}{(\text{atm})\,(\text{atm})^3} = \text{atm}^{-2};\ K_c = (\text{conc})^{-2} = (\text{mol}/l)^{-2}$$

$$\frac{K_p}{K_c} = \frac{\text{atm}^{-2}}{(\text{mol}/l)^{-2}} = \text{atm}^{-2}\, l^{-2} \text{ mol}^2$$

For different reactions, the units for K_p/K_c will be different.

8.4 FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

The equilibrium constant (K) and the standard free energy change (ΔG°) of the reaction are related by the equation:

$$\Delta G^{\circ} = -RT \ln K_p$$

or $$K_p = e^{-\Delta G^{\circ}/RT} \tag{8.10}$$

But $$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$$

$\therefore$ $$K_p = e^{-\Delta G^{\circ}/RT} = e^{-\Delta H^{\circ}/RT}\, e^{\Delta S^{\circ}/R} \tag{8.11}$$

Similarly, $\Delta A^{\circ} = -RT \ln K_c$

or $$K_c = e^{-\Delta A^{\circ}/RT} \tag{8.12}$$

But $$\Delta A^{\circ} = \Delta U^{\circ} - T\Delta S^{\circ}$$

$\therefore$ $$K_c = e^{-\Delta A^{\circ}/RT} = e^{-\Delta U^{\circ}/RT}\, e^{\Delta S^{\circ}/R} \tag{8.13}$$

Here, ΔS° in Eq. (8.11) and Eq. (8.13) is entropy change.

8.5 TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VANT' HOFF EQUATION)

The equilibrium constant may increase, decrease or remain constant with increase in temperature. The temperature dependence of the equilibrium constant is quantitatively given by Equation (8.14), which clearly shows that it depends on standard enthalpy:

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{8.14}$$

If the equilibrium constant changes from K_p (1) to K_p (2) when the temperature changes from T_1 to T_2, then integrating Eq. (8.14) between the appropriate limits gives

$$\int_{K_p(1)}^{K_p(2)} d(\ln K_p) = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2}\, dT$$

Assuming ΔH° independent of T

$$\ln \frac{K_p(2)}{K_p(1)} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

or

$$\log \frac{K_p(2)}{K_p(1)} = -\frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.15}$$

Similarly,

$$\log \frac{K_c(2)}{K_c(1)} = -\frac{\Delta U^\circ}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.16}$$

Here it is assumed that ΔH° (or ΔU°) is independent of temperature, specially for small ranges of temperatures. However, if need be, Kirchhoff's expression can be used for ΔH°.

Equations (8.15) and (8.16) help to calculate the equilibrium constant at T_2 i.e., $K_p(2)$ if $K_p(1)$ at T_1 and ΔH° are known. On the other hand, if equilibrium constants are known at two different temperatures, the average enthalpy of reaction over the temperatures T_1 and T_2 can be calculated. However, if K_p values are known at various temperatures, then ΔH° is calculated graphically from Eq (8.14) which can be written as

$$\ln K_p = -\frac{\Delta H^\circ}{RT} + C' \tag{8.17}$$

where C' is the integration constant. The plot of log K_p versus $1/T$ gives a straight line with slope $\left(= -\frac{\Delta H^\circ}{2.303R}\right)$ i.e.

$$\Delta H^\circ = -2.303R \times \text{slope}$$

Example 8.6 (SI Units) Calculate ΔG° for the following reactions from equilibrium constant values

(a) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$; $K_p = 1.55 \times 10^{15}$ at 298 K

(b) $CO(g) + SO_3(g) \rightleftharpoons CO_2(g) + SO_2(g)$; $K_p = 5.0 \times 10^{24}$ at 400 K

Solution ΔG° is related to K_p as

$$\Delta G^\circ = -RT \ln K_p$$

(a) $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$

$K_p = 1.55 \times 10^{15}$, $T = 298$ K, $R = 8.314$ J K^{-1} mol^{-1}

$$\Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times 2.303 \log (1.55 \times 10^{15})$$
$$= -86.7 \text{ kJ mol}^{-1}$$

(b) $CO(g) + SO_3(g) \rightleftharpoons CO_2(g) + SO_2(g)$

$K_p = 5.0 \times 10^{24}$, $T = 400$ K, $R = 8.314$ J K^{-1} mol^{-1}

$$\Delta G^\circ = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (400 \text{ K}) \times 2.303 \log 5.0 \times 10^{24}$$
$$= -189.2 \text{ kJ mol}^{-1}$$

Example 8.7 (SI Units) The standard free energy of formation at 298 K of $N_2(g)$, $H_2(g)$ and $NH_3(g)$ are 0.0, 0.0 and −16.6 kJ mol^{-1}. Determine the equilibrium constant for the reaction

$$N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$$

Solution ΔG° for the reaction is

$$\Delta G^\circ = 2\Delta G_f^\circ\ (NH_3) - \left[\Delta G_f^\circ\ (N_2) + 3\Delta G_f^\circ\ (H_2)\right]$$

$$= 2\times(-16.6 \text{ kJ mol}^{-1}) - [0+3\times 0]$$

$$= -33.2 \text{ kJ mol}^{-1}$$

Now, $\ln K_p = -\dfrac{\Delta G^\circ}{RT}$

or $\log K_p = -\dfrac{\Delta G^\circ}{2.303\ RT}$

$$\Delta G^\circ = -33.2 \text{ kJ mol}^{-1}, \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}, \quad T = 298\text{K}$$

$$\log K_p = -\frac{-33.2\times 10^3 \text{ J mol}^{-1}}{2.303\times(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\times(298\text{K})}$$

$$= 5.8186$$

$$K_p = 6.59\times 10^5$$

Example 8.8 Equilibrium constant K_p for the reaction

$$H_2(g)+Br_2(g) \rightleftharpoons 2HBr(g)$$

at 25°C is 1.7×10^{19}. Find the free energy of formation of HBr(g) if the free energy of formation ΔG_f° for $Br_2(g)$ and $H_2(g)$ are 0.75 kcal mol^{-1} and 0, respectively.

Solution ΔG° and K_p are related as

$$\Delta G^\circ = -RT \ln K_p$$

$$K_p = 1.7\times 10^{19}, \quad T = 298 \text{ K}, \quad R = 1.98 \text{ cal mol}^{-1} \text{ K}^{-1}$$

$$\Delta G^\circ = -(1.98 \text{ cal mol}^{-1} \text{ K}^{-1})\times(298 \text{ K})\times 2.303 \log(1.7\times 10^{19})$$

$$= -26132 \text{ cal} = -26.132 \text{ kcal mol}^{-1}$$

Now $\Delta G^\circ = 2\Delta G_f^\circ \left[HBr(g)\right] - \left\{\Delta G_f^\circ \left[H_2(g)\right] + \Delta G_f^\circ \left[Br_2(g)\right]\right\}$

$$-26.132 \text{ kcal mo}^{\ 1} = 2\Delta G_f^\circ \left[HBr(g)\right] - \left[0+0.75\right]$$

or $\Delta G_f^\circ \left[HBr(g)\right] = -\ 2.69 \text{ kcal mol}^{-1}$

Example 8.9 (SI Units) The equilibrium constant for the reaction

$$H_2(g)+I_2(g) = 2HI(g) \text{ at } 298 \text{ K}$$

is 16.35. What will be the equilibrium constant at 273 K if the heat of reaction in this temperature range is −25.4 kJ mol^{-1} ?

Solution $\log \dfrac{K_p(2)}{K_p(1)} = -\dfrac{\Delta\ ^\circ}{2.303R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

$$T_1 = 298 \text{ K}, \quad T_2 = 273 \text{ K}, \quad K_p(1) = 16.35,$$

$$\Delta H^\circ = -25.4 \text{ kJ mol}^{-1}$$

$$\log \frac{K_p(2)}{16.35} = -\frac{-25.4\times 10^3 \text{ J mol}^{-1}}{(2.303\times 8.314 \text{ J K}^{-1} \text{ mol}^{-1})}\left[\frac{1}{273}-\frac{1}{298}\right]$$

$$K_p(2) = 41.79$$

Example 8.10 The equilibrium constant K_p for a reaction at 327°C and 347°C are 1×10^{-12} and 5×10^{-12}, respectively. Considering $\Delta H°$ to be constant in the above temperature range, calculate $\Delta H°$ and ΔS for the reaction.

Solution $$\log \frac{K_p(2)}{K_p(1)} = -\frac{\Delta H°}{2.303R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

$K_p(1) = 1\times 10^{-12}$, $K_p(2) = 5\times 10^{-12}$, $T_1 = 327+273 = 600 \text{ K}$,
$T_2 = 347+273=620\text{K}$

$$\log \frac{5\times 10^{-12}}{1\times 10^{-12}} = -\frac{\Delta H°}{2.303\times 1.98}\left[\frac{600-620}{600\times 620}\right]$$

or $\Delta H° = 59.283 \text{ kcal}$

$$\Delta G° = -RT \ln K$$

At 600 K, $K = 1.0\times 10^{-12}$

$$\Delta G° = -1.98\times 600\times 2.303 \log 1.0\times 10^{-12}$$
$$= 32831.6 \text{ cal} = 32.832 \text{ kcal}$$

Now $\Delta G° = \Delta H° - T\Delta S$

or $$\Delta S = \frac{\Delta G° - \Delta H°}{T}$$

$$\Delta S = \frac{32.832 - 59.283}{600}$$
$$= -0.044 \text{ kcal K}^{-1} = -44 \text{ cal K}^{-1}$$

8.6 LE CHATELIER'S PRINCIPLE

Le Chatelier's principle states that when a stress is applied to a system in equilibrium, the position of the equilibrium shifts in such a way as to undo the effect of the stress.

Effect of Concentration

The effect of concentration may be summed up as:
Increase in concentration of any of the *reactants* shifts the equilibrium to the *forward direction.*
Increase in concentration of any of the *products* shifts the equilibrium to the *backward direction.*

Effect of Temperature

Increase of temperature shifts the equilibrium in the direction of the *endothermic reaction* or $\Delta H°$ positive.

Decrease of temperature shifts the equilibrium in the direction of *exothermic reaction* or $\Delta H°$ negative.

Effect of Pressure

Increase in pressure shifts the equilibrium in the direction of *lesser number* of gaseous moles.

Decrease in pressure shifts the equilibrium in the direction of *larger number* of gaseous moles.

Since increase in pressure means decrease in volume, the effect of change of volume will be the reverse of that of pressure.

Effect of Catalyst

A catalyst does not shift the equilibrium in any direction.

Effect of Inert Gas

Introduction of an inert gas in the reaction vessel leads to an increase of total pressure. Therefore, its effect is similar to the increase in total pressure.

8.7 EQUILIBRIA IN HOMOGENEOUS AND HETEROGENEOUS REACTIONS

When in an equilibrium reaction, all the reactants and products are present in one single phase, it is called *homogeneous equilibrium*.
For example,

$$CO(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons CO_2(g) \qquad \text{(all gases)}$$
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \text{(all gases)}$$
$$CH_3COOC_2H_5(l) + 2H_2O(l) \rightleftharpoons C_2H_5OH(l) + CH_3COOH(l) \ \text{(all liquids)}$$

On the other hand, when, in an equilibrium reaction, all the reactants and products are present in two or more phases, it is called a *heterogeneous equilibrium*.
For example,

$$S(s) + O_2(g) \rightleftharpoons SO_2(g)$$
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The equilibrium constants in heterogeneous reactions are defined in exactly the same way as that for homogeneous reactions. For example, for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$K_p = \frac{p_{(CO_2)} \times p_{(CaO)}}{p_{(CaCO_3)}}$$

or

$$K_c = \frac{C_{(CO_2)} \quad C_{(CaO)}}{C_{(CaCO_3)}}$$

However, at a given temperature, the pressure or concentration of a substance, when present in a solid or liquid state, is not included in the expression for the equilibrium constant because the activity of a pure solid or liquid are taken as unity at all temperatures and up to fairly high pressures. Thus,

$$K_p = p_{(CO_2)}$$

or $$K_c = C_{(CO_2)}$$

K_p's of heterogeneous reactions are also called *condensed equilibrium constants*.

EXAMPLE 8.11 Calculate the pressure of CO_2 at 600 K in the reaction, under equilibrium,

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

The standard Gibbs free energies of formation of various substances are

Substance	$CaCO_3(s)$	$CaO(s)$	$CO_2(g)$
ΔG_f° (kJ)	−1128.8	−604.2	−394.4

Solution The free energy change for the reaction

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$\Delta G^\circ = [\Delta G_f^\circ\ (CaO) + \Delta G_f^\circ\ (CO_2)] - \Delta G_f^\circ\ (CaCO_3)$$

$$= [-604.2 + (-394.4)] - (-1128.8)$$

$$= 130.2\ \text{kJ}$$

Now, $$K_p = p_{(CO_2)}$$

$$\log K_p = -\frac{\Delta G^\circ}{2.303\ RT}$$

$$= -\frac{130.2 \times 10^3\ \text{J}}{2.303 \times (8.314\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (600\ \text{K})}$$

$$= -11.3333$$

or $$K_p = 4.64 \times 10^{-12}$$

$$p_{CO_2} = 4.64 \times 10^{-12}\ \text{atm.}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 8.12 (SI Units) The standard Gibbs free energy change for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

is -33.2 kJ mol^{-1} at 298 K

(a) Calculate the equilibrium constant for the above reaction.

(b) What would be the equilibrium constant if the reaction is written as

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

(c) What will be the equilibrium constant for the reaction

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

(d) How are the three equilibrium constants related ?

Solution (a) For the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$\Delta G^\circ = -33.2\ \text{kJ mol}^{-1}.$$

Now, $$\log K_p = -\frac{\Delta G^\circ}{2.303\ RT}$$

$$R = 8.314\ \text{J K}^{-1}\text{mol}^{-1}, \qquad T = 298\text{K},$$

$$\Delta G^\circ = -33.2\times10^3\ \text{J mol}^{-1}$$

$$\log K_p = -\frac{-33.2\times10^3\ \text{J mol}^{-1}}{2.303\times(8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})}$$

$$= 5.8186$$

or $$K_p = 6.59\times10^5$$

(b) For the reaction

$$\tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$\Delta G^\circ = \tfrac{1}{2}\times -33.2 = -16.6\ \text{kJ mol}^{-1}$$

$$\log K_p = -\frac{-16.6\times10^3\ \text{J mol}^{-1}}{2.303\times(8.314\ \text{J K}^{-1}\text{mol}^{-1})\times(298\ \text{K})}$$

$$= 2.91$$

or $$K_p = 811.5$$

(c) For the reaction

$$NH_3(g) \rightleftharpoons \tfrac{1}{2}N_2(g) + \tfrac{3}{2}H_2(g)$$

$$\Delta G^\circ = -[-16.6\ \text{kJ mol}^{-1}] = 16{\cdot}6\ \text{kJ mol}^{-1}$$

$$\log K_p = -\frac{16.6\times10^3\ \text{J mol}^{-1}}{2.303\times(8.314\ \text{J mol}^{-1})\times(298\ \text{K})}$$

$$= -2.91$$

$$K_p = 1.23\times10^{-3}$$

(d) It is clear that $K(b) = K(a)^{1/2}$, i.e, the equilibrium constant with halved coefficients is one-half power of the equilibrium constant for the reaction

$$K(c) = \frac{1}{K(b)}$$

i.e. the equilibrium constant for the reverse reaction is the reciprocal of the equilibrium constant for the forward reaction.

EXAMPLE 8.13 ΔH° and ΔS° for the reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

are 43.14 kcal mol^{-1} and 5.93 cal $\text{K}^{-1}\ \text{mol}^{-1}$, respectively. Calculate the temperature at which the Gibbs free energy is 30 kcal, assuming ΔC_p of the reaction to be zero. What will be the equilibrium constant at this temperature. What will be the percentage conversion of N_2 into NO, starting with an equimolar mixture of N_2 and O_2?

Solution $\Delta C_p = 0$,

Therefore, ΔH° and ΔS° remain constant over the temerature range. Then,

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ$$

$$\Delta G^\circ = 30{,}000\ \text{cal}, \qquad \Delta H^\circ = 43.14\times10^3\ \text{cal},$$

$$\Delta S^\circ = 5.93\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

$$\therefore\quad 30{,}000\ \text{cal} = 43.14\times10^3\ \text{cal} - T\times(5.93\ \text{cal K}^{-1})$$

$$T = 2215.8\ \text{K}$$

Now, $\ln K_p = -\dfrac{\Delta G^\circ}{RT}$

or $\log K_p = -\dfrac{\Delta G^\circ}{2.303\ RT}$

$\Delta G^\circ = 30{,}000$ cal, $R = 1.98$ cal K^{-1} mol^{-1}

$T = 2215.8$ K

$$\log K_p = -\frac{30{,}000}{2.303 \times 1.98 \times 2215.8}$$

or $K_p = 1.07 \times 10^{-3}$

In this case, $K_p = K_c = K_x$

because, $\Delta n = 2 - (1 + 1) = 0$

Let the initial moles for N_2 and O_2 be 1, and x of these be converted into NO, so that at equilibrium,

$$[N_2] = \frac{1-x}{V}, \quad [O_2] = \frac{1-x}{V}, \quad [NO] = \frac{2x}{V}$$

$$K = \frac{4x^2}{(1-x)^2} = 1.07 \times 10^{-3}$$

or $\dfrac{2x}{1-x} = 0.00327$

or $x = 0.00163$

$\therefore$ conversion $= 0.163\%$

Example 8.14 At 267°C, 10.425 g of PCl_5 are heated in a 4 *l* flask. The equilibrium mixture had a pressure of 1 atm. Calculate K_p, K_c and ΔG° for the reaction at 267°C.

Solution

On heating PCl_5 dissociates as, $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$

Initial weight of $PCl_5 = 10.425$ g

$$\text{Moles of } PCl_5 = \frac{10.425}{208.5} = 0.05$$

Let the number of moles of PCl_5 decomposed $= x$

Then, at equilibrium,

Moles of $PCl_5 = 0.05 - x$, Moles of $PCl_3 = x$, Moles of $Cl_2 = x$

Total number of moles $= 0.05 - x + x + x = 0.05 + x$

According to the ideal gas equation

$$\text{Number of moles} = \frac{pV}{RT} = \frac{(1 \text{ atm}) \times (4\ l)}{(0.082 \text{ atm } l \text{ K}^{-1} \text{ mol}^{-1}) \times (540 \text{ K})} = 0.0903$$

or $0.05 + x = 0.0903$

or $x = 0.0403$

$$K_p = \frac{x^2}{a-x} \times \frac{RT}{V} = \frac{(0.0403)^2 \times 0.082 \times 540}{(0.05 - 0.0403) \times 4} = 1.853 \text{ atm}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}}, \quad \Delta n = 1 + 1 - 1 = 1$$

$$\therefore \quad K_c = \frac{1.853}{0.082 \times 540} = 0.0418 \text{ mol } l^{-1}$$

$$\Delta G^\circ = -RT \ln K_p = -1.98 \times 540 \times 2.303 \log 1.853$$
$$= -659.6 \text{ cal}$$

EXAMPLE 8.15 N_2O_4 gas dissociates as

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

At 27°C and 1 atm, 20% of N_2O_4 is dissociated. Calculate

(a) equilibrium constant K_p

(b) per cent dissociation of N_2O_4 at 27°C when the total pressure becomes 0.2 atm

(c) What will be the degree of dissociation when we start with 73.6 g of N_2O_4 in a 10 dm³ vessel at 27°C ?

Solution Let us assume 1 mol of N_2O_4 in the beginning which, according to the equation, dissociates to give 2 mol of NO_2. At 27°C and 1 atm, 20% of N_2O_4 dissociates:

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.	1	0
At equilibrium	$1 - 0.2$ $= 0.8$	0.4

$$\text{Mole fraction of } N_2O_4 \text{ at equilibrium} = \frac{0.8}{0.8 + 0.4} = 0.67$$

$$\text{Mole fraction of } NO_2 \text{ at equilibrium} = \frac{0.4}{0.8 + 0.4} = 0.33$$

Now, total pressure = 1 atm

Partial pressure of $N_2O_4 = 0.67 \times 1 \text{ atm} = 0.67 \text{ atm}$

Partial pressure of $NO_2 = 0.33 \times 1 \text{ atm} = 0.33 \text{ atm}$

$$K_p = \frac{p^2_{(NO_2)}}{p_{(N_2O_4)}} = \frac{(0.33)^2}{0.67}$$
$$= 0.16 \text{ atm}$$

(b) Let α be the degree of dissociation at 0.2 atm pressure

	$N_2O_4 \rightleftharpoons$	$2NO_2$
Initial conc.	1	0
At equilibrium	$1 - \alpha$	2α

$$\text{Partial pressure of } N_2O_4 = \frac{1-\alpha}{1-\alpha+2\alpha} = \frac{1-\alpha}{1+\alpha} \times 0.2 \text{ atm}$$

$$\text{Partial pressure of } NO_2 = \frac{2\alpha}{1+\alpha} \times 0.2 \text{ atm}$$

$$K_p = \frac{p^2_{(NO_2)}}{p_{(N_2O_4)}} = \frac{\left(\dfrac{2\alpha}{1+\alpha} \times 0.2\right)^2}{\left(\dfrac{1-\alpha}{1+\alpha} \times 0.2\right)} = 0.16$$

or
$$\frac{0.8\,\alpha^2}{1-\alpha^2} = 0.16$$

or
$$0.8\alpha^2 = 0.16\,(1 - \alpha^2)$$

Solving, $\alpha = 0.41$, i.e. 41% dissociated at 27°C and 0.2 atm.

(c) Moles of N_2O_4 at the start $= \dfrac{73.6 \text{ g}}{92 \text{ g mol}^{-1}} = 0.80$ mol

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial conc.	0.80		0
At equilibrium	$0.80\,(1 - \alpha)$		1.60α

Partial pressures can be calculated as

$$p_{(N_2O_4)} = \frac{n\,RT}{V}$$

$$= \frac{0.80\,(1-\alpha) \text{ mol} \times (0.082 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1}) \times (300 \text{ K})}{10 \text{ dm}^3}$$

$$= 1.968\,(1 - \alpha) \text{ atm}$$

$$p_{(NO_2)} = \frac{(1.60\alpha \text{ mol}) \times (0.082 \text{ atm dm}^3 \text{ K}^{-1}\text{mol}^{-1}) \times (300 \text{ K})}{10 \text{ dm}^3}$$

$$= 3.936\ \alpha \text{ atm}$$

$$K_p = \frac{p^2_{(NO_2)}}{p_{(N_2O_4)}} = \frac{(3.936\ \alpha)^2}{1.968(1-\alpha)} = 0.16$$

or $\quad 7.872\alpha^2 + 0.16\alpha - 0.16 = 0$

Solving for α, we get

$$\alpha = -\,0.15 \quad \text{or } 0.13$$

Thus, extent of dissociation = 13% (negative value is discarded).

EXAMPLE 8.16 Consider the reaction,

$$2Hg(g) + O_2(g) \rightleftharpoons 2HgO(s)$$

At 327°C, $\Delta H^\circ = -\,71.5$ kcal and $\Delta S^\circ = -\,91.9 \text{ cal K}^{-1} \text{ mol}^{-1}$. The heat capacities at constant pressure are

$$C^\circ_{p,m}\ Hg(g) = 4.95 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$C^\circ_{p,m}\ O_2(g) = 6.31 + 0.0023T \text{ cal K}^{-1}\text{mol}^{-1}$$

$$C^\circ_{p,m}\ HgO(s) = 6.24 + 0.016T \text{ cal K}^{-1}\text{mol}^{-1}$$

Calculate (a) ΔG° and (b) K_p for the above reaction at 27°C.

Solution (a) ΔG° (300 K) can be calculated from the relation

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta\,S^\circ$$

$$\Delta H^\circ(300 \text{ K}) = \Delta H^\circ(600 \text{ K}) + \int_{600}^{300} \Delta C^\circ_p\, dT$$

$$\begin{aligned}\Delta C^\circ_p &= 2C^\circ_p\,(HgO) - 2C^\circ_p\,(Hg) - C^\circ_p\,(O_2)\\ &= 2(6.24 + 0.016T) - 2(4.95) - (6.31 + 0.0023\,T)\\ &= -\,3.73 + 0.0297\,T \text{ cal K}^{-1}\end{aligned}$$

$$\Delta H^\circ(300\text{ K}) = -71.5 - 3.73 \times 10^{-3}(300 - 600) + \tfrac{1}{2} \times 2.97 \times 10^{-5}(300^2 - 600^2)$$
$$= -74.39 \text{ kcal}$$

$$\Delta S^\circ(300\text{ K}) = \Delta S^\circ(600\text{ K}) + \int_{600}^{300} \frac{\Delta C_p^\circ}{T}\, dT$$

$$= -91.9 - 3.73 \ln \frac{300}{600} + 0.0297\,(300 - 600)$$
$$= -98.22 \text{ cal K}^{-1}$$
$$\Delta G^\circ = \Delta H^\circ(300\text{ K}) - T\,\Delta S^\circ(300\text{ K})$$
$$= -74.39 - 300\,(-98.22 \times 10^{-3})$$
$$= -44.92 \text{ kcal}$$

(b) $$\log K_p = -\frac{\Delta G^\circ}{2.303\,RT}$$

$\Delta G^\circ = -44.92$ kcal, $R = 1.98$ cal K^{-1}mol^{-1},
$T = 300$ K

$$\log K_p = \frac{44.92}{2.303 \times 1.98 \times 300}$$
$$= 32.84$$
$$\therefore \quad K_p = 6.86 \times 10^{32}$$

QUESTIONS

Numerical Problems

8.1 A gaseous reaction between hydrogen and iodine giving hydrogen iodide at 400°C in a 5 dm^3 flask contain 0.4 mol of hydrogen, 0.4 mol of iodine and 2.4 mol of hydrogen iodide.

(a) Calculate the equilibrium constant for the reaction.

(b) What will be the equilibrium constant for the reverse reaction ?

8.2 PCl_5 decomposes into PCl_3 and Cl_2. It is found that if we put 3 mol of PCl_5 in a 2 l flask and heat at 350°C, 40% of it decomposes. Calculate the equilibrium constants K_c and K_p for the reaction.

8.3 (SI Units) Calculate the ratio of K_p to K_c at 300 K for the following reactions :

(a) $2SO_3\,(g) \rightleftharpoons 2SO_2\,(g) + O_2\,(g)$

(b) $2H_2S\,(g) + 3O_2\,(g) \rightleftharpoons 2H_2O\,(g) + 2SO_2\,(g)$

(c) $H_2\,(g) + Br_2\,(g) \rightleftharpoons 2HBr\,(g)$.

8.4 (SI Units) Three moles of acetic acid and two moles of ethyl alcohol are refluxed at 373 K till equilibrium is reached. Analysis at equilibrium showed that 1.5 mol of acetic acid was left unreacted.

(a) What is the equilibrium constant for the reaction ?

(b) What is ΔG° for the reaction ?

(c) How many moles of acetic acid will be present if, initially 5 mol of it are taken ?

8.5 (SI Units) Write the expression for the equilibrium constant K_p for the following reactions and calculate K_p from the ΔG° values:

(a) $CrCl_3\ (s) + \frac{1}{2}H_2\ (g) \rightleftharpoons CrCl_2\ (s) + HCl\ (g)$; $\Delta G^\circ\ (1000\ K) = -51.8\ kJ$

(b) $SO_2\ (g) + \frac{1}{2}O_2\ (g) \rightleftharpoons SO_3\ (g)$; $\Delta G^\circ\ (900\ K) = -14.07\ kJ$

(c) $H_2\ (g) + Br_2\ (g) \rightleftharpoons 2HBr\ (g)$; $\Delta G^\circ\ (298\ K) = -109.5\ kJ.$

8.6 (SI Units) The standard Gibbs free energy change for the reaction

$$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$$

is -4.86 kJ at 298 K.

(a) Calculate the equilibrium constant for the above reaction.

(b) What would be the equilibrium constant if the reaction is written as

$$NO_2\ (g) \rightleftharpoons \tfrac{1}{2}N_2O_4\ (g)$$

(c) What will be the equilibrium constant for the reaction

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

(d) How are the three equilibrium constants related ?

8.7 K_p for the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

at 25°C is 0.14.

(a) A flask at 25°C initially contains pure N_2O_4 at 10 atm. What will be the partial pressure of N_2O_4 and NO_2 after equilibrium ?

(b) What is ΔG° for the reaction ?

(c) What is ΔG at equilibrium ?

(d) Calculate K_x for the reaction.

8.8 In the reaction

$$NH_3 \rightleftharpoons \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$

at equilibrium at 450°C and 10 atm, the partial pressures of N_2 and H_2 are 2.44 and 7.35 atm, respectively. Calculate the equilibrium constants (a) K_p (b) K_c and (c) K_x for the reaction.

8.9 In the equilibrium mixture of

$$CO(g) + Br_2\ (g) \rightleftharpoons COBr_2\ (g)$$

the partial pressure of CO(g), Br_2 (g) and $COBr_2$ (g) are found to be 0.208 atm, 0.134 atm and 0.092 atm at 47°C.

(a) Calculate K_p for the reaction.

(b) What is ΔG° for the reaction ?

8.10 (SI Units) At 1 atm and 673 K, ΔG° for the reaction

$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2\ (g)$$

is -16.95 kJ mol^{-1}. Calculate the degree of dissociation of phosgene ($COCl_2$) into CO(g) and Cl_2(g), at the same temperature and pressure.

8.11 Nitrosyl bromide is 34% dissociated at 27°C and total pressure is 0.25 atm, at equilibrium.

$$2NOBr\ (g) \rightleftharpoons 2NO(g) + Br_2\ (g)$$

Calculate K_p and ΔG° for the dissociation.

8.12 PCl_5 is 40% dissociated at 327°C and 1 atm pressure

$$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$$

(a) Calculate K_p for the reaction.

(b) Calculate the degree of dissociation at a total pressure of 5 atm.

8.13 (SI Units) For the reaction

$$2HI(g) \rightleftharpoons H_2\ (g) + I_2\ (g)$$

$\Delta H^\circ = 10\ kJ\ mol^{-1}$ and $\Delta S^\circ = -22.0\ J\ K^{-1}\ mol^{-1}$ at 1000 K and 1.01×10^5 $N\ m^{-2}$. Calculate K_p for the reaction.

8.14 The vapour density of PCl_5 when in equilibrium with its dissociation products was found to be 90.

(a) Calculate its degree of dissociation.

(b) Calculate the dissociation constant of PCl_5 at this temperature if the pressure is 1 atm.

8.15 The equilibrium constant for the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

at 627°C is 3.16×10^3. SO_2 and O_2 are introduced in stoichiometric ratio in a 1 *l* flask at 627°C at an initial pressure of 3 atm. What percentage of SO_2 is converted to SO_3 ?

8.16 For a decomposition reaction of the type

$$A_2 \rightleftharpoons 2A$$

K_p at 1025 K and 1.01×10^5 N m^{-2} is exactly twice the K_p at 1000 K and the same pressure. Calculate ΔH° for this reaction in this temperature range.

8.17 The equilibrium constant for the reaction

$$N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$$

at 25°C is 6.0×10^5. Calculate the equilibrium constant for the reaction at 50°C. ΔH° in this temperature range is -92.0 kJ (assume ΔH° to be independent of temperature).

8.18 The equilibrium constant for the reaction

$$A_2 \rightleftharpoons 2A$$

was found to be 636 at 50°C. Calculate the degree of dissociation of A_2 when the pressure of the reaction mixture is 182 mm of Hg. At what pressure will the dissociation be 50% ?

8.19 (SI Units) Calculate K_p for the reaction, at 298 K,

$$CO_2\,(g) + H_2\,(g) \rightleftharpoons CO(g) + H_2O(g)$$

from the following data:

$\Delta G_f^\circ\,(CO_2) = -\,394.4$ kJ mol^{-1} $\qquad \Delta G_f^\circ\,(H_2) = 0$

$\Delta G_f^\circ\,(CO) = -\,137.3$ kJ mol^{-1} $\qquad \Delta G_f^\circ\,(H_2O) = -\,228.6$ kJ mol^{-1}.

8.20 The plots of log K_p against $1/T$ are straight lines for the following reactions. Determine ΔH° for these reactions from the given slopes:

(a) $CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2\,(g)$; $\qquad$ Slope $= -\,8.10 \times 10^3$

(b) $SO_2\,(g) + \frac{1}{2}O_2\,(g) \rightleftharpoons SO_3\,(g)$; $\qquad$ Slope $= 4.95 \times 10^3$

8.21 (SI Units) Find the equilibrium constant K_p for the reaction

$$CH_4\,(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2$$

from the following data :

	$-\,(G^\circ - H_o^\circ)/T$ J K^{-1} mol^{-1}	H_o° kJ mol^{-1}
$CH_4\,(g)$	199.05	-150.54
$H_2O(g)$	196.65	-238.49
$CO(g)$	201.67	-190.50
$H_2\,(g)$	136.98	0

8.22 The dissociation constant of $CaCO_3$ at 900°C and 1000°C are 800 mm and 2950 mm, respectively. Calculate the heat of dissociation in this temperature range (assuming it to be independent of temperature).

8.23 Calculate the fraction of methane decomposed at 1 atm pressure and 727°C if the reaction is

$$CH_4(g) \rightleftharpoons C(s) + 2H_2\,(g)$$

$(G^\circ - H_0^\circ)/T$ for $CH_4(g) = -47.65$, for $C(s) = -\,2.77$ and for $H_2(g) = -\,32.74$ cal mol^{-1}K^{-1}

$\Delta H_0^\circ = 15.98$ kcal.

8.24 (SI Units) (a) Calculate the equilibrium constant K_p for the reaction:

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

at 800 K and 1.01×10^5 Pa, given that

$\Delta G_f^\circ\,[Fe(s)] = -\,21.6$ kJ mol^{-1}; $\qquad \Delta G_f^\circ\,[H_2O(g)] = -\,390$ kJ mol^{-1},

$\Delta G_f^\circ\,[Fe_3O_4\,(s)] = -\,1236.0$ kJ mol^{-1} and $\Delta G_f^\circ\,[H_2(g)] = -\,106.8$ kJ mol^{-1}.

(b) What will be the ratio of pressure of H_2O to that of H_2 at 800 K ?

8.25 (SI Units) For the reaction

$3\,Fe_2O_3(s) \rightleftharpoons 2Fe_3O_4 + \frac{1}{2}O_2(g)$

$\Delta H^\circ(298\text{ K}) = 230.6\text{ kJ mol}^{-1}$ and $\Delta G^\circ = 196.5\text{ kJ mol}^{-1}$

(a) Calculate the equilibrium constant for the reaction at 298 K.

(b) Calculate the equilibrium constant for the reaction at 328 K (assuming ΔH° to be independent of temperature in this range).

QUIZ QUESTIONS

Type A: Multiple Choice

8.26 When a system is at equilibrium

(a) the concentration of the reactants and the products become equal

(b) the rate of the backward reaction becomes very low

(c) the rate of the forward and backward reactions become equal

(d) the opposing reactions (backward and forward) stop

8.27 At equilibrium, the free energy change (ΔG) for a reaction is

(a) zero

(b) always negative

(c) infinite

(d) maximum

8.28 The standard state Gibbs free energy change (ΔG°) is related to equilibrium constant K_p as

(a) $K_p = -RT\ln\Delta G^\circ$

(b) $K_p = \left(\frac{e}{RT}\right)^{-\Delta G^\circ}$

(c) $K_p = -\frac{\Delta G^\circ}{RT}$

(d) $K_p = e^{-\Delta G^\circ/RT}$

8.29 In the two gaseous reactions (i) and (ii), at 25°C,

(i) $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g)$ $\quad K_1$

(ii) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ $\quad K_2$

the equilibrium constants K_1 and K_2 are related as

(a) $K_2 = \frac{1}{K_1}$ (b) $K_2 = \frac{K_1}{2}$

(c) $K_2 = \frac{1}{K_1^2}$ (d) $K_2 = K_1^2$

8.30 Equilibrium constants K_p and K_c are related as

(a) $K_c = K_p\,(RT)^{\Delta n}$

(b) $K_p = K_c\,(RT)^{\Delta n}$

(c) $K_p = \left(\frac{K_c}{RT}\right)^{\Delta n}$

(d) $K_p - K_c = (RT)^{\Delta n}$

8.31 The variation of K_p with temperature can be given by Vant' Hoff's equation as

(a) $\log\frac{K_p(2)}{K_p(1)} = -\frac{\Delta U^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(b) $\log\frac{K_p(2)}{K_p(1)} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(c) $\log\frac{K_p(1)}{K_p(2)} = -\frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(d) $\log\frac{K_p(2)}{K_p(1)} = -\frac{\Delta H^\circ}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

Type B: Multiple Choice (Numerical Problems)

8.46 Four moles of A are mixed with four moles of B when 2 mol of C are formed at equilibrium, according to the reaction

$$A + B \rightleftharpoons C + D$$

The value of the equilibrium constant is

(a) $\frac{1}{4}$
(b) $\frac{1}{2}$
(c) 1
(d) 4

8.47 For the gaseous reaction

$$A_2(g) \rightleftharpoons 2A(g)$$

the equilibrium constant at 125 K is 10^2. The approximate value of ΔG° is (assume $R = 8.0$ J mol^{-1}K^{-1})

(a) −23.03 kJ
(b) −100 kJ
(c) −4.606 kJ
(d) −2.303 kJ

8.48 ΔG° for the reaction

$$A + B \rightleftharpoons C$$

is − 4.606 kcal. The approximate value of the equilibrium constant for the reaction at 227°C is (assume $R = 2$ cal mol^{-1} K ^{1})

(a) 100
(b) 1.202×10^{-6}
(c) 10
(d) data are not sufficient for calculation

8.49 For the reaction

$$C(s) + CO_2\,(g) \rightleftharpoons 2CO\,(g)$$

an equilibrium mixture had partial pressures, for CO_2 and CO, of 4.0 and 8.0 atm, respectively. K_p for the reaction is

(a) 0.5
(b) 2
(c) 16
(d) 32

8.50 The equilibrium constant K_p for a reaction

$$\tfrac{1}{2}A_2(g) + B_2(g) \rightleftharpoons AB_2(g)$$

at 127°C and 227°C are 1×10^{-12} and 1×10^{-11}, respectively. The enthalpy of the reaction is (assume ΔH to be independent of temperature in this range and $R \approx 2$ cal mol^{-1} K^{-1})

(a) 230.3 cal
(b) 4.606 kcal
(c) 689.3 kcal
(d) 9.212 kcal

8.51 The equilibrium concentration of the components in a reaction

$A + B \rightleftharpoons C + D$ are

[A] = 2 mol l^{-1}
[B] = 4 mol l^{-1}
[C] = 10 mol l^{-1}
[D] = 8 mol l^{-1}

ΔG° for the reaction at 27°C is ($R \approx 2$ cal mol^{-1} K^{-1})

(a) − 600 cal
(b) − 1382 cal
(c) − 691 cal
(d) 1160 cal

8.52 Eight moles of a gas AB_3 are introduced into a previously evacuated 1 dm^3 container in which it dissociates as

$$2AB_3(g) \rightleftharpoons A_2(g) + 3B_2(g)$$

At equilibrium, 2 mol of A_2(g) are present. The equilibrium constant K_c is

(a) 72 mol^2 l^{-2}
(b) 36 mol^2 l^{-2}
(c) 3 mol^2 l^{-2}
(d) 27 mol^2 l^{-2}

8.53 K_c for the reaction

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

at 373 K is 4.0×10^9 dm³ mol⁻¹. The K_c for the reaction

$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$

at 373 K will be

(a) 2.5×10^{-9} mol dm^{-3}
(b) 2.5×10^{-10} mol dm^{-3}
(c) 2.5×10^{-10} mol^{-1} dm^{3}
(d) 2.5×10^{-8} mol^{-1} dm^{3}

8.54 K_c for the reaction

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

at 300 K is 4.0×10^{-6}. K_p for the above reaction will be ($R = 2$ cal mol^{-1} K^{-1})

(a) 2.4×10^{-3}
(b) 4×10^{-6}
(c) $4 \times 10^{-6}\,(RT)^2$
(d) 16×10^{-12}

8.55 For the reaction

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$

the concentrations of the equilibrium mixture at 27°C are

$[N_2O_4] = 4.8 \times 10^{-2}$ mol l^{-1}
$[NO_2] = 1.2 \times 10^{-2}$ mol l^{-1}

K_c for the reaction is

(a) 0.25
(b) 3×10^{-1} mol l^{-1}
(c) 3×10^{3} mol l^{-1}
(d) 3×10^{-3} mol l^{-1}

8.56 In the two gaseous equilibria (i) and (ii), at a certain temperature,

(i) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ K_1
(ii) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ K_2

If K_1 is 4×10^{-3} then K_2 will be

(a) 8×10^{-3}
(b) 16×10^{-6}
(c) 6.25×10^{4}
(d) 6.25×10^{8}

8.57 Initially, 0.8 mol of PCl_5 and 0.2 mol of PCl_3 are mixed in a one-litre vessel. At equilibrium, 0.4 mol of PCl_3 is present. The value of K_c for the reaction

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

would be

(a) 0.05 mol l^{-1}
(b) 0.13 mol l^{-1}
(c) 0.013 mol l^{-1}
(d) 0.66 mol l^{-1}

8.58 In an equilibrium mixture for the reaction

$CO + 2H_2 \rightleftharpoons CH_3OH$

at 427°C the partial pressures of CH_3OH, CO and H_2 are 2, 1 and 0.1 atm respectively. K_p *for the decomposition of methanol to* CO *and* H_2 *is*

(a) 200 atm^{-2} (b) 20 atm^{-1}
(c) 5×10^{-3} atm^{2} (d) 50 atm^{2}

8.59 When 3 mol of ethyl alcohol are mixed with 3 mol of acetic acid, 2 mol of ester are formed at equilibrium according to the equation

$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

The value of the equilibrium constant for the reaction is

(a) 4 (b) 2/9 (c) 2 (d) 4/9

8.60 ΔG° for a reaction is 46.06 kcal. K_p for the reaction at 27°C is

(a) 33.3 (b) $10^{-33.3}$

(c) 0.2×10^{-10} (d) 3.33×10^{-2}

Type C: True or False

8.61 The rate of the reverse reaction becomes more than the forward reaction after attaining the state of equilibrium.

8.62 The equilibrium constant for the reaction between H_2 and I_2 is independent of pressure.

8.63 A catalyst does not disturb the equilibrium.

8.64 The value of the equilibrium constant is not affected by the direction from which equilibrium is attained.

8.65 At equilibrium, ΔG must be negative.

8.66 For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ the numerical value of K_p is equal to K_c.

8.67 The reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; $\Delta H = +43$ kcal, is favoured by increase of temperature as well as pressure.

8.68 The effect of introduction of an inert gas in the reaction vessel is similar to an increase in total pressure.

8.69 At equilibrium, the rate of the forward reaction becomes zero while rate of the backward reaction is not zero.

8.70 Increase in pressure has no effect on the reaction $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$.

Type D: Fill in the Blanks

Consider the reaction

$$2H_2S(g) + 3O_2(g) \rightleftharpoons 2H_2O(g) + 2SO_2(g) \qquad \Delta H^\circ = -237 \text{ kJ}$$

State the effect (increase, decrease, no change) that the specified change will have on the original equilibrium value of the quantity given in column (2).

	(1) Change	(2) Equilibrium value	(3) Effect
8.71	Increasing pressure	Moles of SO_2	
8.72	Increasing pressure	Moles of O_2	
8.73	Increasing temperature	Moles of SO_2	
8.74	Decreasing temperature	Moles of H_2S	
8.75	Adding inert gas	Moles of H_2O	
8.76	Adding catalyst	Magnitude of K	
8.77	Increasing volume	Moles of H_2O	
8.78	Decreasing temperature	Magnitude of K	
8.79	Removing water (condensation)	Moles of SO_2	
8.80	Adding H_2S	Moles of O_2	

ANSWERS

Numerical Problems

8.1 (a) 36 (b) 2.8×10^{-2} *8.2* $K_c = 0.4$ mol l^{-1}, $K_p = 20.43$ atm *8.3* (a) 2.494×10^3 J mol^{-1} (b) 4.0×10^{-4} J^{-1} mol (c) 1 *8.4* (i) 3 (ii) —3.407 kJ (iii) 3.3 mol *8.5* (a) 5.07×10^2 (b) 6.55 (c) 1.55×10^{19} *8.6* (a) $K_p = 7.108$ (b) $K_p = 2.67$ (c) $K_p = 0.14$ (d) $K_b = (K_a)^{1/2}$; $K_c = 1/K_a$ *8.7* (a) $p(N_2O_4) = 9.43$ atm, $p(NO_2) = 1.14$ atm (b) 1160.3 cal (c) 0 (d) 0.014 *8.8* (a) 148.05 (b) 2.50 (c) 14.80 *8.9* (a) 3.30 atm (b) —756.6 cal *8.10* 20% *8.11* 1.3×10^{-2}, 10.8 kJ *8.12* (a) 0.19 (b) 19.1% *8.13* 2.13×10^{-2} *8.14* 0.0256 *8.15* 42.6% *8.16* 236.3 kJ *8.17* 1.596×10^3 *8.18* 0.68%, 0.477 mm *8.19* 1.01×10^{-5} *8.20* (a) 36.94×10^3 cal mol^{-1} (b) -22.6×10^3 cal mol^{-1} *8.21* 26.91 *8.22* 19.5 kcal *8.23* 85% *8.24* (a) 198.6 (b) 0.27 *8.25* (a) 3.7×10^{-35} (b) 1.86×10^{-31}

Quiz Questions

8.26 (c) *8.27* (a) *8.28* (d) *8.29* (c) $K_1 = \frac{[NO_2]}{[NO]\,[O_2]^{\frac{1}{2}}}$, $K_2 = \frac{[NO]^2\,[O_2]}{[NO_2]} = \frac{1}{K_1{}^2}$ *830* (b) *8.31* (d) *8.32* (c) *8.33* (a) *8.34* (a) *8.35* (c) *8.36* (d) *8.37* (b) It can be shown that $K_p = \frac{x^2 p}{1-x^2}$: If x is small in comparison to 1 so that $1-x^2 \approx 1$ and $K_p = x^2 p$ or $x^2 \propto 1/p$ or $x \propto \sqrt{1/p}$ *8.38* (c) *8.39* (b) *8.40* (a) *8.41* (d) *8.42* (c) *8.43* (d) *8.44* (b) *8.45* (c) *8.46* (c) At equilibrium $[A] = [B] = 4-2$ and $[C] = [D] = 2$ so that $K = 1$ *8.47* (c) $\Delta G^\circ = -\,2.303\,RT \log K = -2.303 \times 8 \times 8 \times 125 \times \log 10^2 = 4.606$ kJ *8.48* (a) *8.49* (c): $K_p = \frac{p(CO)^2}{p(CO_2)} = \frac{(8.0)^2}{4.0} = 16$ atm *8.50* (d) *8.51* (b): $K = \frac{(10.0) \times (8.0)}{(2.0) \times (4.0)} = 10$, $\Delta G^\circ = -2.303 \times 2 \times 300 \times \log 10 = 1.38$ kcal *8.52* (d) *8.53* (b) Equilibrium constant $= \frac{1}{4.0 \times 10^9} = 2.5 \times 10^{-10}$ mol l^{-1} *8.54* (b) *8.55* (d) *8.56* (c) *8.57* (b) *8.58* (c) *8.59* (d) *8.60* 9 *8.61* False: A reaction does not stop at equilibrium. Rather, equilibrium is dynamic *8.62* True *8.63* True *8.64* True *8.65* False: At equilibrium $\Delta G = 0$ *8.66* True *8.67* False: Reaction is favoured by increase in temperature but pressure has no effect. *8.68* False *8.69* False *8.70* False *8.71* increase *8.72* decrease *8.73* decrease *8.74* decrease *8.75* increase *8.76* no effect *8.77* decrease *8.78* decrease *8.79* increase *8.80* decrease.

9

Liquids and their Properties

Liquids have definite volumes but not definite shapes. In this state, the intermolecular forces are strong enough to hold the molecules together but thermal forces are also large enough to impart translational motion to the molecules. The nature and magnitude of intermolecular forces decide the structure of a liquid and also its characteristic properties. These properties include vapour pressure, surface tension, viscosity, refractive index, etc.

9.1 VAPOUR PRESSURE

The vapour pressure of a liquid at a given temperature is the pressure exerted by the vapours present above the liquid in equilibrium with liquid at the same temperature.

The vapour pressure is a characteristic property of a liquid at a given temperature. It does not depend upon the amount of the liquid or the vapour phase. The vapour pressure of a liquid increases exponentially with rise in temperature.

The temperature at which the vapour pressure of the liquid becomes equal to the external pressure (i.e. the atmospheric pressure) is called the *normal boiling point* of the liquid. If the external pressure is large, the boiling point will be correspondingly higher.

The amount of heat required to convert one mole of the liquid into its vapour, at a given temperature, is called the *enthalpy of vaporisation* of the liquid. The greater the attractive forces present in a liquid, the larger is the enthalpy of vaporisation. It can be estimated from the Clausius-Clapeyron equation, from pressures p_1 and p_2 at temperatures T_1 and T_2, as

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{evap}}}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{9.1}$$

or

$$\Delta H_{\text{evap}} = 2.303\,R\left[\frac{T_1\,T_2}{T_2 - T_1}\right] \log \frac{p_2}{p_1} \tag{9.2}$$

Here, we assume that the gaseous phase behaves ideally.

The boiling point (T_b) is related to the heat of vaporisation (ΔH_{evap}) and critical temperature (T_c) by the approximate empirical relations:

$$\frac{\Delta H_{\text{evap}}}{T_b} \approx 21 \text{ cal K}^{-1}\text{ mol}^{-1} \quad \text{(Trouton's rule)}$$

$$\text{or} \qquad \approx 85 \text{ J K}^{-1}\text{ mol}^{-1} \quad \text{(SI Units)} \qquad (9.3)$$

It may be noted that Trouton's rule is applicable only for unassociated liquids.

$$T_b \approx \frac{2}{3}\, T_c \quad \text{(Guldberg's rule)} \qquad (9.4)$$

The vapour pressure of a liquid can be determined by either of the two methods, *static* or *dynamic.*

EXAMPLE 9.1 The vapour pressures of water at 95°C and 100°C are 634 and 760 mm of Hg, respectively. Calculate the mean enthalpy of vaporisation between 95°C and 100°C.

Solution The enthalpy of vaporisation

$$\Delta H_{\text{evap}} = 2.303\, R\left(\frac{T_1\, T_2}{T_2 - T_1}\right) \log \frac{p_2}{p_1}$$

$$T_1 = 273+95 = 368 \text{ K}, \qquad T_2 = 273+100 = 373 \text{ K}$$

$$p_1 = 634 \text{ mm of Hg}, \qquad p_2 = 760 \text{ mm of Hg}$$

$$\Delta H_{\text{evap}} = 2.303 \times 1.98 \left(\frac{368 \times 373}{373-368}\right) \log \frac{760}{634}$$

$$= 9.85 \text{ kcal mol}^{-1}$$

EXAMPLE 9.2 Vapour pressure of benzene at 20°C is 75.6 torr. Calculate the vapour pressure at 30°C. The enthalpy of vaporisation of benzene = 7.353 kcal mol^{-1}.

Solution

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{evap}}}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$p_1 = 75.6 \text{ torr}, \qquad T_1 = 273+20 = 293 \text{ K},$$

$$T_2 = 273+30 = 303 \text{ K}$$

$$\Delta H_{\text{evap}} = 7.353 \text{ kcal mol}^{-1}$$

$$\therefore \quad \log \frac{p_2}{75.6} = \frac{7.353 \times 10^3}{1.98 \times 2.303}\left(\frac{303-293}{303 \times 293}\right)$$

$$= 0.1816$$

$$\text{or} \qquad \frac{p_2}{75.6} = 1.5191$$

$$p_2 = 114.8 \text{ torr}$$

9.2 SURFACE TENSION

A molecule in the bulk of a liquid is surrounded by more molecules than one on the surface. As a consequence, the free energy of a molecule is more on the surface than in the bulk. This is why work has to be done when a molecule is brought from the bulk to the surface phase in a liquid. Alternatively, we may say that the liquid surface is under tension due to unbalanced forces. Whenever we want to stretch the surface, work has to be done against this tension, which is called the surface tension. If it is an interface between two bulk liquids, it is called interfacial tension. Surface tension, may be defined as the force per unit length acting perpendicular to the tangential line on the surface.

The units of surface tension are force per unit length, i.e. dyn cm^{-1} (in SI units, newton per metre, N m^{-1}) and is usually denoted by γ.

The work done in increasing the surface area by one unit area is called *surface free energy* and has the units erg cm^{-2} (in SI units, joule per square metre, J m^{-2}).

Surface tension or surface energy is due to the intermolecular interactions between molecules, and therefore liquids with stronger intermolecular forces will have large surface tensions. The surface tension of liquids decrease with increase of temperature. Among the empirical relations of temperature dependence of surface tension, the important one is the *Evotos relation*

$$\gamma = \left(\frac{p}{M}\right)^{2/3} K\,(T_c - T) \tag{9.5}$$

where K is a constant and γ becomes zero at $T = T_c$.

The commonly used methods for the determination of surface tension are:

The Capillary Rise Method

If a capillary tube is placed in a liquid which wets its surface, then the liquid rises in the capillary. The height to which the liquid rises depends on the surface tension of the liquid and the radius of the capillary. From the height (h) and radius of the capillary (r), γ can be calculated as

$$\gamma = \tfrac{1}{2}\, h\, \rho\, g \tag{9.6}$$

where ρ is density and g is the acceleration due to gravity.

If the liquid does not wet the glass and θ is the angle of contact between the liquid and the capillary, then

$$\gamma = \frac{rh\,\rho\,g}{2\cos\theta} \tag{9.7}$$

The Drop Weight or Drop Number Method

This method is based upon the principle that a drop falling from a tube or a capillary has two types of forces acting on it; the surface tension force acting upward and the gravitational force acting downward. If two liquids have surface tensions γ_1 and γ_2 and drop weights are m_1 and m_2, then

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2} \tag{9.8}$$

If we count the number of drops from the same volume, then

$$\frac{\gamma_1}{\gamma_2} = \frac{\rho_1 n_2}{\rho_2 n_1} \tag{9.9}$$

where n_1 and n_2 are the number of drops for the liquids whose densities are ρ_1 and ρ_2 respectively.

Du Nouy's tensiometer

This is a commercial method in which tension on the dial of the torsion head, which is directly proportional to the surface tension of the liquid is measured. If τ_1 and τ_2 are the tensions for two liquids whose surface tensions are γ_1 and γ_2, then

$$\frac{\gamma_1}{\gamma_2} = \frac{\tau_1}{\tau_2} \tag{9.10}$$

Surface Active Agents

There are many substances which, when dissolved in a liquid, lower its surface tension. Such substances are called surface active agents. Lowering of surface tension is due to the adsorption of the molecules of the surface active substance on the surface of the liquid. For example, alcohols, fatty acids and amines lower the surface tension of water.

Interfacial Tension

If two immiscible or partially miscible liquids are taken in a vessel, the force acting per unit length perpendicular to the imaginary line in the interface is called the interfacial tension. For liquids which do not interact very strongly, the interfacial tension is nearly equal to the difference in their surface tensions.

9.3 SURFACE TENSION AND CHEMICAL CONSTITUTION

Surface tension is related to density by the Macleod relationship:

$$\frac{\gamma^{1/4}}{\rho - \rho'} = C \tag{9.11}$$

where ρ is the density of the liquid, ρ' is the density of the saturated vapours of the liquid at the same temperature and C is a constant.

$$\frac{M\gamma^{1/4}}{\rho - \rho'} = \text{parachor } (P) \tag{9.12}$$

At ordinary temperatures, ρ' is very small in comparison to ρ so that

$$\frac{M\gamma^{1/4}}{\rho} = P$$

or

$$V\gamma^{1/4} = P \tag{9.13}$$

Thus, *parachor* is the molecular volume of the liquid at a temperature at which its surface tension is unity. Parachor is an additive property and has been useful in deciding between different alternative structures of compounds. However, with the availability of a number of modern structure-determining methods, its use is limited.

Example 9.3 In an experiment at 20°C, water rose in a capillary of diameter 0.076 cm to a height of 3.92 cm. Calculate the surface tension of water if the density of water at this temperature is 0.998 g cm^{-3} and $g = 981$ cm s^{-2}.

Solution The surface tension

$$\gamma = \tfrac{1}{2} rh \rho g \qquad \text{(Assuming } \theta = 0)$$

$$r = 0.076/2 = 0.038 \text{ cm}, \qquad h = 3.92 \text{ cm},$$

$$g = 981 \text{ cm s}^{-2}, \qquad \rho = 0.998 \text{ g cm}^{-3}$$

$$\gamma = \tfrac{1}{2} \times (0.038 \text{ cm}) \times (3.92 \text{ cm}) \times (0.998 \text{ g cm}^{-3}) \times (981 \text{ cm s}^{-2})$$

$$= 72.92 \text{ g s}^{-2} = 72.92 \text{ dyn cm}^{-1}$$

$$[1 \text{ dyn} = 1 \text{ g cm s}^{-2}]$$

Example 9.4 (SI Units) How high will water rise in a capillary of radius 2.0×10^{-4} m at 293 K ? (For water $\gamma = 72.75 \times 10^{-3}$ N m^{-1}, $g = 9.81$ m s^{-2}, $\rho = 1.0 \times 10^3$ kg m^{-3}.)

Solution

$$\gamma = \tfrac{1}{2} r \rho hg$$

$$h = \frac{2\gamma}{r \rho g}$$

$$r = 2.0 \times 10^{-4} \text{ m}, \qquad \rho = 1.0 \times 10^3 \text{ kg m}^{-3}$$

$$\gamma = 72.75 \times 10^{-3} \text{ N m}^{-1} \qquad g = 9.81 \text{ m s}^{-2}$$

$$h = \frac{2 \times (72.75 \times 10^{-3} \text{ N m}^{-1})}{(2.0 \times 10^{-4} \text{ m}) \times (1.0 \times 10^3 \text{ kg m}^{-3}) \times (9.81 \text{ m s}^{-2})}$$

$$= 0.074 \text{ N s}^2 \text{ kg}^{-1} \quad 1 \text{ N} = 1 \text{ kg m s}^{-2}]$$

$$\therefore \qquad h = 0.074 \text{ m}$$

Example 9.5 Fifty drops each, of water and ether, weigh 3.64 g and 0.852 g, respectively. Determine the surface tension of ether if the surface tension of water is 72.75 dyn cm^{-1}.

Solution $\dfrac{\gamma_1}{\gamma_2} = \dfrac{m_1}{m_2}$

Weight of one drop of water $(m_1) = \dfrac{3.64}{50}$

Weight of one drop of ether $(m_2) = \dfrac{0.852}{50}$

$$\gamma_1 = 72.75 \text{ dyn cm}^{-1}$$

$$\gamma_2 = \frac{\gamma_1 \times m_2}{m_1}$$

$$= \frac{(72.75 \text{ dyn cm}^{-1}) \times \left(\dfrac{0.852}{50} \text{ g}\right)}{\left(\dfrac{3.64}{50} \text{ g}\right)}$$

$$= 17.03 \text{ dyn cm}^{-1}$$

EXAMPLE 9.6 (SI Units) The number of drops of water, counted in a drop-number method from a stalagmometer, is 100 whereas the number of drops for an organic liquid is 280. What is the surface tension of the organic liquid if the surface tension of water is 0.07275 N m^{-1} and the densities of water and the organic liquid are 0.998×10^3 kg m^{-3} and 0.755×10^3 kg m^{-3} respectively ?

Solution $$\frac{\gamma_1}{\gamma_2} = \frac{n_2 \rho_1}{n_1 \rho_2}$$

or $$\gamma_2 = \frac{\gamma_1 n_1 \rho_2}{n_2 \rho_1}$$

$$\gamma_1 = 0.07275 \text{ N m}^{-1}, \quad n_1 = 100, \quad n_2 = 280,$$

$$\rho_1 = 0.998 \times 10^3 \text{ kg m}^{-3}$$

and $$\rho_2 = 0.755 \times 10^3 \text{kg m}^{-3}$$

$$\gamma_2 = \frac{(0.07275 \text{ N m}^{-1}) \times 100 \times (0.755 \times 10^3 \text{ kg m}^{-3})}{280 \times (0.998 \times 10^3 \text{ kg m}^{-3})}$$

$$= 0.01966 \text{ N m}^{-1}$$

9.4 VISCOSITY

Viscosity is the internal resistance to flow, in liquids, which one layer offers to another layer trying to pass over it. The force of friction required to maintain a constant difference of velocity (v) between two layers, each having area A cm^2 separated by a distance x, is

$$f \propto \frac{Av}{x} = \eta \frac{Av}{x} \tag{9.14}$$

where η is called the *coefficient of viscosity*. It may be defined as the tangential force per unit area required to maintain a unit velocity gradient.

The units of the coefficient of viscosity or simply viscosity are poise (P), where 1 P = 1 g cm^{-1} s^{-1} = 1 dyn s cm^{-2} (in SI units 1 P = 0.1 N s m^{-2}). The viscosity of a liquid decreases with increase in temperature. Arrhenius (1912) observed that viscosity depended on temperature according to the relation :

$$\eta = A\, e^{\Delta E_{\text{vis}}/RT} \tag{9.15}$$

or $$\log \eta = \log A + \frac{\Delta E_{\text{vis}}}{2.303\, RT} \tag{9.16}$$

It can be seen that a graph between log η and $1/T$ should be a straight line with a slope $B = \Delta E_{\text{vis}}/2.303\text{R}$ where ΔE_{vis} is the activation energy for the viscous flow.

The flow of liquid through a capillary tube of length l and radius r can be derived from Poiseuille's equation and expressed as

$$\eta = \frac{\pi r^4 \Delta pt}{8\, Vl} \tag{9.17}$$

where V is the volume of liquid flowing in t seconds and p is the pressure difference maintained at the two ends of the tube.

Viscosity can be measured with the help of a viscometer. Ostwald's viscometer is generally used. It consists of a U tube with bulbs blown in each limb. A known volume of liquid is introduced in the viscometer within fixed marks. It is then allowed to flow under its own weight (hydrostatic pressure) and time of flow is noted. The accurate measurement of η with Eq. (9.17) is difficult and, in practice, a relative method is used as

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2} \tag{9.18}$$

η_1 is calculated if the times of flow t_1 and t_2 and densities ρ_1 and ρ_2 for the two liquids are measured and η_2 is known.

For solutions, the ratio of the viscosity of the solution (η) to that of the pure solvent (η_0) is called relative viscosity (η_r), i.e.,

$$\text{Relative viscosity, } \eta_r = \frac{\eta}{\eta_0}$$

The specific viscosity, η_{sp} is defined as

$$\eta_{sp} = \eta_r - 1 = \frac{\eta - \eta_0}{\eta_0}$$

The value of η_{sp}/C obtained by extrapolating the plot of η_{sp}/C to zero concentration is known as intrinsic viscosity, $[\eta]$, *i.e.*,

$$[\eta] = \lim_{C \to 0} (\eta_{sp}/C)$$

9.5 VISCOSITY AND CHEMICAL CONSTITUTION

Viscosity can help to predict whether the liquid is associated or not. Dunstan observed that for non-associated liquids

$$\frac{\rho}{M} \eta \times 10^6 = 40 \text{ to } 70 \tag{9.19}$$

and for associated liquids the value is much higher than 70.

EXAMPLE 9.7 The times of flow for the same volume of water and carbon tetrachloride, through an Ostwald's viscometer, are 400 and 275 seconds, respectively. The densities of water and carbon tetrachloride are 0.998 and 1.542 g cm^{-3} respectively. What is the viscosity coefficient of CCl_4 if the value for water is 0.01002 P ?

Solution $$\frac{\eta_1}{\eta_2} = \frac{t_1 \rho_1}{t_2 \rho_2}$$

$$\eta_1 = 0.01002 \text{ P}, \quad t_1 = 400 \text{ s}, \quad t_2 = 275 \text{ s}$$

$$\rho_1 = 0.998 \text{ g cm}^{-3} \quad \rho_2 = 1.542 \text{ g cm}^{-3}$$

Coefficient of viscosity for CCl_4

$$\begin{aligned}\eta_2 &= \frac{\eta_1 \times t_2 \times \rho_2}{t_1 \times \rho_1}\\ &= \frac{(0.01002\ \mathrm{P}) \times (275\ \mathrm{s}) \times (1.542\ \mathrm{g\ cm^{-3}})}{(400\ \mathrm{s}) \times (0.998\ \mathrm{g\ cm^{-3}})}\\ &= 0.01064\ \mathrm{P}\end{aligned}$$

EXAMPLE 9.8 (SI Units) The viscosity of olive oil at 293 K is $0.084\ \mathrm{N\ s\ m^{-2}}$, and its density is $1.1 \times 10^3\ \mathrm{kg\ m^{-3}}$. How long will it take to pass through a viscometer if water under the same conditions takes 30 s ? (viscosity of water = $0.00101\ \mathrm{N\ s\ m^{-2}}$, density = $0.998 \times 10^3\ \mathrm{kg\ m^{-3}}$).

Solution

$$\frac{\eta_1}{\eta_2} = \frac{t_1\,\rho_1}{t_2\,\rho_2}$$

$$\eta_1 = 0.084\ \mathrm{N\ s\ m^{-2}}, \quad \rho_1 = 1.10 \times 10^3\ \mathrm{kg\ m^{-3}}, \quad t_1 = ?$$

$$\eta_2 = 0.00101\ \mathrm{N\ s\ m^{-2}}, \quad \rho_2 = 0.998 \times 10^3\ \mathrm{kg\ m^{-3}} \quad t_2 = 30\ \mathrm{s}$$

$$\begin{aligned}t_1 &= \frac{\eta_1\,t_2\,\rho_2}{\eta_2\,\rho_1} = \frac{(0.084\ \mathrm{N\ s\ m^{-2}}) \times (0.998 \times 10^3\mathrm{kg\ m^{-3}}) \times (30\mathrm{s})}{(0.00101\ \mathrm{N\ s\ m^{-2}}) \times (1.1 \times 10^3\ \mathrm{kg\ m^{-3}})}\\ &= 2263.7\ \mathrm{s}\end{aligned}$$

or $\quad = 37\ \mathrm{min}\ 43.7\ \mathrm{s}$

9.6 REFRACTIVE INDEX

The refractive index of a medium is defined as the ratio of the speed of light in the medium to that in the vacuum i.e. refractive index

$$n = \frac{\text{velocity of light in medium}}{\text{velocity of light in vacuum}} \qquad (9.20)$$

It is more convenient to measure the refractive index with respect to air than with respect to vacuum. The refractive index of air at atmospheric pressure relative to vacuum is 1.00029.

Snell's Law

If a beam of light enters from a less dense medium into a denser medium at an incident angle i and is refracted at an angle r, then, according to Snell's law,

$$\frac{\sin i}{\sin r} = \frac{n_1}{n_2}$$

where n_2 is the refractive index of the less dense medium and n_1 is the refractive index of the denser medium.

Refractive index is measured in the laboratory with a refractometer. Two common refractometers are: (i) Pulfrich refractometer and (ii) Abbe's refractometer.

9.7 SPECIFIC REFRACTION OR MOLAR REFRACTION

Attempts have been made to relate the chemical constitution of a substance with its refractive index. Lorenz and Lorentz (1880) defined a new term, specific refraction R, as

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{1}{\rho} \tag{9.21}$$

It has been found that specific refraction is almost independent of temperature.

The molar refraction (refractivity) is defined as

$$R_m = \frac{M}{\rho}\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{9.22}$$

The molar refractivity is an additive and constitutional property and helps to decide the correct structure.

EXAMPLE 9.9 The refractive index of carbon tetrachloride is 1.4573 and its density is 1.595 g cm^{-3}. Calculate its molar refraction.

Solution Molar refraction,

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{\rho}$$

$$n = 1.4573, \quad \rho = 1.595 \text{ g cm}^{-3}, \quad M = 154 \text{ g mol}^{-1}$$

$$\therefore \quad R_m = \frac{154}{1.595}\left[\frac{(1.4573)^2 - 1}{(1.4573)^2 + 2}\right]$$

$$= 26.31 \text{ cm}^3 \text{ mol}^{-1}$$

9.8 OPTICAL ROTATION

The electric field associated with a light beam vibrate in all planes at right angles to the direction of propagation. However, when it is passed through a Nicol prism, its vibrations are restricted to one plane only. Such a light beam is called *plane polarised light*.

The substances which can rotate the plane of the polarised light are called *optically active substances*. If the plane is rotated to the right, the substance is called *dextrorotatory* and if it is rotated to the left, it is called *levorotatory*.

For solutions the rotation of the plane of polarised light depends upon the length of the liquid column through which the light is allowed to pass, its concentration and nature. It is expressed by

$$R = [\alpha]_\lambda^T \frac{ml}{V} \tag{9.23}$$

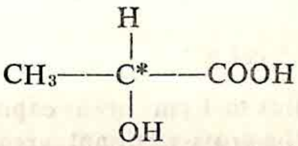
where l is the length in decimetres, m is the weight of the optically active substance dissolved in volume V, and $[\alpha]_\lambda^T$ is the specific rotation of the substance which depends upon the temperature and wavelength of the light used besides the nature of the substance. It may be defined as the angle of rotation of the plane polarised light when it passes through 1 dm of a solution containing 1 g of substance per cm³ of the solution. If the optically active substance itself is a liquid and is used as such, then M/V is equal to density, and we have

$$[\alpha]_{\lambda}^{T} = \frac{R}{l\,\rho} \tag{9.24}$$

The optical activity is measured with an instrument called a *polarimeter*.

9.9 OPTICAL ACTIVITY AND CHEMICAL CONSTITUTION

Optical activity is purely a constitutive property, i.e. it depends upon the arrangement of atoms within the molecule. It has been found that compounds which are optically active contain at least one carbon atom to which four different atoms or groups are attached. Such a carbon atom is called an *asymmetric* carbon atom. For example, lactic acid,



$$CH_3\text{---}\overset{\displaystyle H}{\underset{\displaystyle OH}{C^*}}\text{---}COOH$$

has one asymmetric carbon atom (C*).

A general criterion of an optically active substance is that its mirror image cannot be superimposed on the original molecule. The optical activity can be used to test the presence of asymmetry in the molecule.

Example 9.10 A solution of a certain optically active substance in water, containing 4.2 g in 25 ml, is introduced in a 20 cm long polarimeter tube. It rotated polarised light by 6.2°. Calculate the specific rotation.

Solution

$$[\alpha]_{\lambda}^{T} = \frac{RV}{l\,m}$$

$R = 6.2°, \quad V = 25 \text{ ml}, \quad m = 4.2 \text{ g}, \quad l = 20 \text{ cm} = 2 \text{ dm}$

$$[\alpha]_{\lambda}^{T} = \frac{6.2 \times 25}{2 \times 4.2} = 18.45°$$

MISCELLANEOUS EXAMPLES

Example 9.11 The vapour pressure of chloromethane is given by the relation

$$\log p\,(\text{mm}) = 7.482 - \frac{1150.0}{T} \tag{i}$$

Calculate (a) the normal boiling point
(b) the enthalpy of vaporisation per gram.

Solution (a) The normal boiling point is the temperature at which the vapour pressure of the liquid becomes equal to atmospheric pressure, i.e. 760 mm Hg.

$$\log p = 7.482 - \frac{1150.0}{T}$$

$$\therefore \quad \log 760 = 7.482 - \frac{1150.0}{T}$$

or $$\frac{1150}{T} = 7.482 - \log 760 = 4.6012$$

$$\therefore \quad T = 249.9\ \text{K} = -23.1°\text{C}$$

(b) Comparing Eq. (i) with Clausius-Clapeyron equation of the form

$$\log p = \text{constant} - \frac{\Delta H_{\text{evap}}}{2.303\ RT}$$

and $$\log p = 7.482 - \frac{1150}{T}$$

$$\frac{\Delta H_{\text{evap}}}{2.303R} = 1150$$

$$\Delta H_{\text{evap}} = 1150 \times 2.303 \times 1.98 = 5243.9\ \text{cal mol}^{-1}$$

$$M(CH_3Cl) = 50.5$$

$$\therefore \quad \Delta H_{\text{evap}} = \frac{5243.9}{50.5} = 103.8\ \text{cal g}^{-1}$$

EXAMPLE 9.12 An organic liquid rises to 1 cm in a capillary tube of radius r. How much will it rise if the cross-sectional area of the capillary tube is (i) doubled and (ii) reduced to half?

Solution The cross-sectional area of the capillary tube $= \pi r^2$

If cross-sectional area of one capillary is a_1, then

$$a_1 = \pi r_1^2$$

or $$r_1 = \sqrt{\frac{a_1}{\pi}}$$

For the second capillary,

$$a_2 = 2a_1 = \pi r_2^2$$

or $$r_2 = \sqrt{\frac{2a_1}{\pi}}$$

Now $\gamma = \frac{1}{2}\, g\, h\, r\, \rho$

i.e. for the same liquid

$$\frac{h_2}{h_1} = \frac{r_1}{r_2}$$

If $h_1 = 1$ cm

$$h_2 = \frac{\sqrt{a_1/\pi}}{\sqrt{2a_1/\pi}} \times 1 = \frac{1}{\sqrt{2}} = 0.707\ \text{cm}$$

(ii) If cross-sectional area is reduced to half, then

$$a_3 = \frac{a_1}{2} = \pi r_3^2$$

or $$r_3 = \sqrt{\frac{a_1}{2\pi}}$$

Now, $$\frac{h_3}{h_1} = \frac{r_1}{r_3}$$

If $h_1 = 1$ cm.

$$h_3 = \frac{\sqrt{a_1/\pi}}{\sqrt{a_1/2\pi}} = \sqrt{2} = 1.414\ \text{cm}$$

EXAMPLE 9.13 A glass capillary of diameter 0.10 cm is dipped into (a) water and (b) mercury. Calculate the level of the liquid in the capillary in each case from the following data:

Surface tension of water = 72.75 dyn cm^{-1}, Density = 0.9984 g cm^{-3}

Surface tension of mercury = 480 dyn cm^{-1}, Density = 13.6 g cm^{-3}

Contact angle for water = 10°, and for mercury = 140°.

Solution Surface tension,

$$\gamma = \frac{rh\rho g}{2\cos\theta}$$

or

$$h = \frac{2\gamma\cos\theta}{r\rho g}$$

(a) For water, $r = 0.10/2 = 0.05$ cm. $\rho = 0.9984 \text{ g cm}^{-3}$

$g = 980.6 \text{ cm s}^{-2}$ $\gamma = 72.75 \text{ dyn cm}^{-1}$

$\theta = 10^\circ$, $\cos 10^\circ = 0.9848$

$$h = \frac{2\times(72.75 \text{ dyn cm}^{-1})\times(0.9848)}{(0.05 \text{ cm})\times(0.9984 \text{ g cm}^{-3})\times(980.6 \text{ cm s}^{-2})}$$
$$= 2.93 \text{ cm}$$

Water rises to a height of 2.93 cm

(b) For mercury, $r = 0.05$ cm, $\rho = 13.6 \text{ g cm}^{-3}$, $g = 980.6 \text{ cm s}^{-2}$, $\gamma = 480 \text{ dyn cm}^{-1}$, $\theta = 140^\circ$, $\cos 140^\circ = -0.7660$

$$h = \frac{2\times(480 \text{ dyn cm}^{-1})\times(-0.7660)}{(0.05 \text{ cm})\times(13.6 \text{ g cm}^{-3})\times(980.6 \text{ cm s}^{-2})} = -1.10 \text{ cm}$$

Mercury depresses by 1.10 cm

EXAMPLE 9.14 The density of hexane at 25°C is 0.6874 g cm^{-3}. Calculate the surface tension of hexane if the parachors of ethane and propane are 110.5 and 150.8, respectively.

Solution The parachor values

$$[P]_{C_2H_6} = 110.5, \quad [P]_{C_3H_8} = 150.8$$
$$[P]_{CH_2} = [P]_{C_3H_8} - [P]_{C_2H_6} = 150.8 - 110.5$$
$$= 40.3$$
$$[P]_{C_6H_{14}} = [P]_{C_3H_8} + 3\,[P]_{CH_2}$$
$$= 150.8 + 3 \times 40.3 = 271.7$$

Molecular weight of hexane $(M) = 86$

Surface tension is related to parachor as

$$\frac{M\gamma^{1/4}}{\rho} = P$$

or

$$\gamma^{1/4} = \frac{[P]\,\rho}{M}$$

$P = 271.7$, $M = 86$, $\rho = 0.6874 \text{ g cm}^{-3}$

$$\gamma^{1/4} = \frac{271.7\times0.6874}{86}$$

or

$$\gamma = \left(\frac{271.7\times0.6874}{86}\right)^4$$
$$= 22.01 \text{ dyn cm}^{-1}$$

EXAMPLE 9.15 The coefficient of viscosity for benzene at various temperatures are given below:

$t(^\circ C)$	0	20	40	60	80
$\eta(P)$	0.00912	0.00652	0.00503	0.00392	0.00329

(a) Calculate the activation energy for viscous flow.
(b) Calculate the viscosity at 30°C.

Solution

(a) The coefficient of viscosity varies with temperature as

$$\log \eta = A + B/T$$

where A and B are constants. Value of B can be calculated as slope of $\log \eta$ versus $1/T$ as

$T(K)$	273	293	313	333	353
$1/T$	3.663×10^{-3}	3.41×10^{-3}	3.20×10^{-3}	3.00×10^{-3}	2.83×10^{-3}
η	0.00912	0.00652	0.00503	0.00392	0.00329
$\log \eta$	−2.04	−2.186	−2.298	−2.407	−2.483

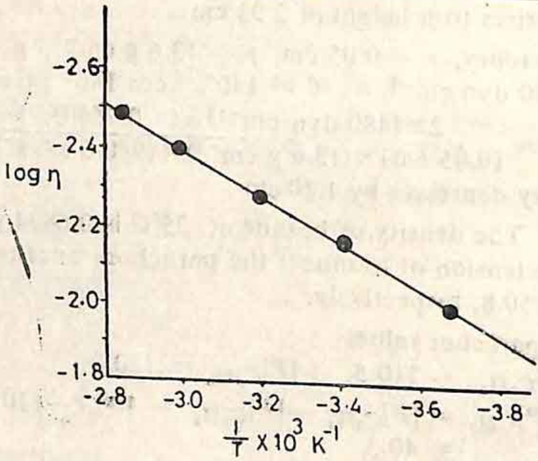


Fig. 9.1 Graph of $\log \eta$ *vs* $1/T \times 10^3$.

The plot of $\log \eta$ and $1/T$ (Fig. 9.1) gives slope $B = 0.514 \times 10^3$ K

$$\therefore \quad \Delta E_{vis} = 2.303\, R\, B$$

$$= 2.303 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (0.514 \times 10^3 \text{ K})$$

$$= 9.84 \text{ kJ mol}^{-1}$$

(b) The value of A can be calculated at any temperature. Let us calculate at 20°C, $\log \eta = -2.186$, $B = 0.514 \times 10^3$, $T = 293$ K

$$A = \log \eta - \frac{B}{T} = -2.186 - \frac{0.514 \times 10^3}{293} = -3.940$$

η at 30°C can be calculated as

$$\log \eta = A + \frac{B}{T} = -3.940 + \frac{0.514 \times 10^3}{298}$$

$$= -2.215$$

$$\therefore \quad \eta = 6.093 \times 10^{-3} = 0.006093 \text{ P}.$$

QUESTIONS

Numerical Problems

9.1 The vapour pressures of a substance at 300 K and 310 K are 90 and 110 mm Hg, respectively. What is its enthalpy of vaporisation ?

9.2 A liquid boils at 73°C at 1 atm. What will be its boiling point under a pressure of 700 mm Hg if its enthalpy of vaporisation is 9 kcal mol^{-1} ?

9.3 The vapour pressure of water at 90°C is 526 mm Hg and the mean enthalpy of vaporisation between 90° and 110°C is 542 cal g^{-1}. Calculate the vapour pressure of water at 110°C.

9.4 (SI Units) The surface tension of water at 293 K is 72.75×10^{-3} N m^{-1}. How high will water rise in a capillary of diameter 0.01 cm ?

9.5 Mercury in a capillary tube of diameter 0.08 cm suffers a depression of 14 mm. Calculate the surface tension of mercury if the angle of contact of mercury is 140° and density is 13.6 g cm^{-3} ($g = 980.6$ cm s^{-2}).

9.6 (SI Units) The surface tension of toluene at 323 K is 88% of its value at 293 K. If the capillary rise is 1.2 cm at 293 K, what is the rise in capillary at 323 K in the same capillary assuming expansion of glass to be negligible ?

9.7 The surface tension of a liquid at 27°C is 27.1 dyn cm^{-1} and its density at this temperature is 0.9880 g cm^{-3}. What is the radius of the largest capillary that will allow the liquid to rise 2.0 cm (assume the angle of contact to be zero and $g = 981$ cm s^{-2}) ?

9.8 (SI Units) The surface tension of water at 293 K is 72.75×10^{-3} N m^{-1} and of ethanol is 22.3×10^{-3} N m^{-1}, at the same temperature. How much less, in the same capillary, will alcohol rise in comparison to water ? Density of ethanol $= 0.9614 \times 10^3$ kg m^{-3} and density of water $= 0.9982 \times 10^3$ kg m^{-3}.

9.9 The tensions in the du Nouy tensiometer for two liquids *A* and *B*, are 26 and 37 respectively. What will be the surface tension of *B* if the value for *A* is 26.5 dyn cm^{-1} ?

9.10 The density of acetone at 20°C is 0.7910 g ml^{-1}. Calculate the surface tension of acetone given that the parachor equivalent of C, H, O and the double bond are 7.2, 16.2, 20.0 and 23.2, respectively.

9.11 The number of drops of water counted in a stalagmometer at 25°C is 300 whereas the number of drops for ethanol is 314. Calculate the surface tension of ethanol given that the density of water = 0.9980 g cm^{-3}, density of ethanol = 0.9614 g cm^{-3} and surface tension of water = 72.75 dyn cm^{-1}.

9.12 In an experiment with Poiseuille's apparatus, the following data were obtained:

Volume of liquid flowing per min = 20 cc
Length of tube = 25 cm
Radius of tube = 1 mm
Pressure difference maintained = 73.5×10^3 dyn cm^{-2}

Calculate the coefficient of viscosity.

9.13 In a measurement of viscosity with the Ostwald viscometer, water takes 580 s to flow through a given volume, while an organic liquid takes 395 s. Calculate the viscosity of organic liquid. Densities of organic liquid and water are 0.7867 and 0.9984 g cm^{-3}, respectively. Viscosity of water is 1.01 cP.

9.14 Compare the time of flow of the same volume of 20% wt sucrose solution (density $= 1.0794 \times 10^3$ kg m^{-3} and $\eta = 1.695$ cP) and 30% wt sucrose solution (density $= 1.1252 \times 10^3$ kg m^{-3} and $\eta = 2.735$ cP).

9.15 What is the volume of a liquid that will flow in 20 min through a capillary 20 cm long and of 1 mm diameter ? The viscosity of the liquid is 0.10 poise and the pressure difference at the two ends of the capillary is 2 atm.

9.16 The coefficient of viscosity for C_2H_5OH at various temperatures are given below:

$t(°C)$	0	20	40	60
$\eta \times 10^2 (P)$	1.773	1.200	0.834	0.592

(a) Calculate the activation energy for viscous flow.
(b) Calculate the viscosity at 30°C.

9.17 The following data are given at 20°C:
Density of water = 0.9983 g cm^{-3}, Viscosity of water = 1.0087 cP
Density of acetone = 0.7910 g cm^{-3}, Viscosity of acetone = 0.3290 cP
Which of the two liquids is associated ?

9.18 (SI Units) How long will a machine oil take to pass through a viscometer if water under same conditions takes 1 min ?
Density of water = 1.0×10^3 kg m^{-3} $\eta = 0.00101$ N s m^{-2}
Density of oil = 0.97×10^3 kg m^{-3}, $\eta = 0.060$ N s m^{-2}

9.19 A substance having the molecular formula C_3H_6O may be allyl alcohol ($CH_2 = CH-CH_2OH$) or acetone (CH_3COCH_3). Determine the correct formula if the observed molar refractivity of the compound is 15.998 cm^3 mol^{-1}. Given that refractivities for C = 2.418, H = 1.100, O (carbonyl) = 2.211, O (hydroxyl) = 1.525 and C = C bond = 1.733.

9.20 The molar refraction for a liquid is 12.95 cm^3 mol^{-1} and its density is 1.046 g cm^{-3}. Calculate the refractive index (mol. mass of liquid is 60).

9.21 The refractive index of a liquid at 25°C is 1.5 and its density is 0.87 g cm^{-3}. Find the molar refraction.

9.22 Calculate the specific rotation of plane polarised sodium D light when it passes through an aqueous solution of lactose (13 g per 100 ml) in a 10 cm cell and gives a rotation of 7.25°.

9.23 Calculate the optical rotation when sodium D light passes through a solution of a compound in chloroform, containing 15 g per 100 ml, placed in a cell of 10 cm. $[\alpha]_6^{25}$ for the compound in chloroform is + 37.5°.

9.24 Water rose in a capillary to a height of 4.8 cm at 25°C. The density of water at 25°C is 0.9984 g cm^{-3}. The same capillary, when filed with mercury, contained 40.5 mg/cm of the capillary. Calculate the surface tension of water (Density of mercury = 13.6 g cm^{-3} and $g = 980.6$ g s^{-2}).

9.25 Normal hexane boils at 68°C. Assuming that it obeys Trouton's rule, estimate its vapour pressure at 25°C.

QUIZ QUESTIONS

Type A: Multiple Choice

9.26 The vapour pressure of a liquid
(a) always increases with temperature
(b) always decreases with temperature
(c) is independent of temperature
(d) increases only up to the boiling point

9.27 Liquids diffuse slowly as compared to gases because
(a) liquids have no fixed shape
(b) the molecules of liquids are heavy
(c) the mean free path of the molecules of liquids is very short
(d) the molecules are held together by strong intermolecular forces

9.28 With rise in temperature surface tension of a liquid
(a) increases
(b) decreases
(c) remains constant
(d) increases only up to 100°C

9.29 When evaporation and condensation rates become equal in a closed bottle containing a liquid,
(a) cooling will be caused
(b) the state is called the critical state
(c) the amounts of the substance in the liquid and vapour states become constant
(d) the amounts of the substance in the liquid and vapour states become equal

9.30 The Trouton rule may be expressed as
(a) $\frac{\Delta H_{\text{evap}}}{T_{\text{boiling}}} \approx 21 \text{ cal K}^{-1} \text{ mol}^{-1}$
(b) $T_{\text{boiling}} \approx 2/3\ T_{\text{critical}}$
(c) $\frac{M\gamma^{1/4}}{\rho} = \text{Parachor}$
(d) $\eta = A\ e^{\Delta E/RT}$

9.31 The units of surface tension in the SI system are
(a) dynes per cm
(b) N m^{-1}
(c) N m^2
(d) p

9.32 The rise of a liquid in a capillary tube is due to
(a) osmosis
(b) surface tension
(c) viscosity
(d) diffusion

9.33 The units of surface energy in CGS system are
(a) dyn/cm^2
(b) erg/cm^2
(c) cal
(d) cal/deg

9.34 In the drop-number method, if we take two liquids whose surface tensions are γ_1 and γ_2, number of drops n_1 and n_2, and densities ρ_1 and ρ_2, then
(a) $\frac{\gamma_1}{\gamma_2} = \frac{\rho_2 n_2}{\rho_1 n_1}$
(b) $\frac{\gamma_1}{\gamma_2} = \frac{\rho_2 n_1}{\rho_1 n_2}$
(c) $\frac{\gamma_1}{\gamma_2} = \frac{\rho_1 n_2}{\rho_2 n_1}$
(d) $\frac{\gamma_1}{\gamma_2} = \frac{\rho_1 n_1}{\rho_2 n_2}$

9.35 In the du Nouy tensiometer, if T_1 and T_2 are the tensions on the dial of the torsion head for two liquids whose surface tensions are γ_1 and γ_2, then, from the known value of γ_1, γ_2 can be calculated as
(a) $\gamma_2 = \frac{T_1}{T_2} \times \gamma_1$
(b) $\gamma_2 = \gamma_1 (T_2 - T_1)$
(c) $\gamma_2 = \frac{T_2}{T_1} \times \gamma_1$
(d) $\gamma_2 = \gamma_1 \left(1 - \frac{T_2}{T_1}\right)$

9.36 In the CGS system, the units of coefficient of viscosity are
(a) erg cm^{-2}
(b) dyn cm^{-2}
(c) poise cm^{-2}
(d) dyn s cm^{-2}

9.37 If ρ is the density of the liquid and ρ' is the density of the vapour at the same temperature, then the parachor $[P]$ may be expressed as

(a) $[P] = \dfrac{M\gamma}{\rho - \rho'}$

(b) $[P] = \dfrac{M\gamma^{1/4}}{\rho - \rho'}$

(c) $[P] = \dfrac{M\gamma^{1/2}}{\rho' - \rho}$

(d) $[P] = \gamma\left(\dfrac{M}{\rho - \rho'}\right)^{2/3}$

9.38 The internal resistance to flow possessed by a liquid is called its

(a) interfacial tension
(b) fluidity
(c) viscosity
(d) surface tension

9.39 The force of friction (f) between two cylindrical layers each of area a cm², separated by l cm and having a velocity difference of v cm s⁻¹, is given by

(a) $f = \eta\, a\, v\, l$

(b) $f = \dfrac{av}{l\eta}$

(c) $f = \eta\, \dfrac{av}{l}$

(d) $f = \eta\, \dfrac{lv}{a}$

9.40 With increase in temperature, the fluidity of liquids

(a) increases
(b) decreases
(c) remains constant
(d) may increase or decrease

9.41 If η_1 and η_2 are the coefficients of viscosity of two liquids, ρ_1 and ρ_2 their densities and t_1 and t_2 the flow times in Ostwald viscometer, then

(a) $\dfrac{\eta_1}{\eta_2} = \dfrac{\rho_1 t_2}{\rho_2 t_1}$

(b) $\dfrac{\eta_1}{\eta_2} = \dfrac{\rho_2 t_2}{\rho_1 t_1}$

(c) $\dfrac{\eta_1}{\eta_2} = \dfrac{\rho_1 t_1}{\rho_2 t_2}$

(d) $\dfrac{\eta_1}{\eta_2} = \dfrac{\rho_2 t_1}{\rho_1 t_2}$

9.42 If η and η_0 are the coefficients of viscosity of a solution and the pure solvent, then specific viscosity may be expressed as

(a) η/η_0 (b) $\dfrac{\eta - \eta_0}{\eta_0}$

(c) $\dfrac{\eta_0 - \eta}{\eta_0}$ (d) $\dfrac{\eta + \eta_0}{1 - \eta_0}$

9.43 The refractive index of a medium is defined as

(a) velocity of light in vacuum/velocity of light in medium
(b) velocity of light in medium/velocity of light in air
(c) velocity of light in medium − velocity of light in vacuum
(d) velocity of light in medium/velocity of light in vacuum

9.44 If n and ρ are the refractive index and density of the liquid and M molar mass, then molar refraction is defined as

(a) $R_m = \dfrac{M}{\rho}\left(\dfrac{n^2 - 1}{n^2 + 2}\right)$

(b) $R_m = \frac{M}{\rho}\left(\frac{n^2 -}{n^2 + 1}\right)$

(c) $R_m = \frac{M}{\rho}\left(\frac{n^2 - 1}{n^2 - 2}\right)$

(d) $R_m = \frac{1}{M\rho}\left(\frac{n^2 - 1}{n^2 + 2}\right)^2$

9.45 The rotation of plane polarised light when it passes through 1 dm of a solution containing 1 g of substance per cm^3 of the solution is called
(a) specific refraction
(b) specific rotation
(c) molar refraction
(d) rheochor

9.46 If R is the rotation of plane polarized light when passed through a liquid column of density ρ, then specific rotation is equal to
(a) $R \times l \times \rho$
(b) $R \times l/\rho$
(c) $\frac{R}{l \times \rho}$
(d) $\frac{R \times \rho}{l}$

9.47 The molecule which is optically inactive due to internal compensation is called
(a) an enantiomer
(b) levorotatory
(c) a meso compound
(d) an enantiomorph

9.48 Which of the following properties increase with the increase of temperature ?
(a) vapour pressure
(b) surface tension
(c) viscosity
(d) both surface tension and fluidity

9.49 If a liquid of density ρ rises in a capillary of radius r cm to a height of h cm, and θ is the contact angle, then the surface tension of the liquid is
(a) $\frac{1}{2} r\, h\, \rho\, g \cos\theta$
(b) $\frac{2\cos\theta}{r\, h\, \rho\, g}$
(c) $\frac{r\, h\, \rho\, g}{2\cos\theta}$
(d) $\frac{2\, r\, h\, \rho\, g}{\cos\theta}$

9.50 For associated liquids, the value of $\frac{\rho}{M}\,\eta \times 10^6$ should be (where ρ is density, M molar mass and η coefficient of viscosity),
(a) zero
(b) between 40 to 70
(c) infinite
(d) higher than 70

Type B : Multiple Choice (Numerical Problems)

9.51 Fifty drops of water and an organic liquid weigh 3.64 and 0.728 g, respectively. The surface tension of liquid is (surface tension of water = 72.8 dyn cm^{-1})
(a) 364 dyn cm^{-1}
(b) 36.4 dyn cm^{-1}
(c) 1.456 dyn cm^{-1}
(d) 14.56 dyn cm^{-1}

9.52 The number of drops of water and an organic liquid, in a drop-number method from a stalagmometer are 100 and 200, respectively. Calculate γ for the organic liquid if γ for $H_2O = 72.8$ dyn cm^{-1}, density of water is 1.00 g cm^{-3} and density of organic liquid is 0.90 g cm^{-3}.
(a) 131.04 dyn cm^{-1}
(b) 65.52 dyn cm^{-1}
(c) 32.76 dyn cm^{-1}
(d) 72.8 dyn cm^{-1}

9.53 The heat of vaporization of benzene is 7353 cal mol^{-1}. The approximate boiling point of benzene is
(a) 77.1°C
(b) 350.1°C
(c) 201.6°C
(d) 623.1°C

9.54 The flow time for water ($\rho = 1$ g cm^{-3}, $\eta = 0.008$ P) in the Ostwald viscometer is 240 s at 25°C. If 160 s are required for the same volume of organic liquid *X* ($\rho = 0.9$ g cm^{-3}) to flow, then η for the liquid is
(a) 0.00148 P
(b) 0.005170 P
(c) 0.002585 P
(d) 0.002980 P

9.55 A liquid *X* rose in a capillary of diameter 0.02 cm to a height of 2 cm. The surface tension of liquid is (density of liquid = 1.5 g cm^{-3} $g = 980$ cm s^{-2})
(a) 19.6 dyn cm^{-1}
(b) 39.2 dyn cm^{-1}
(c) 29.4 dyn cm^{-1}
(d) 14.7 dyn cm^{-1}

9.56 A solution of an optically active substance, containing 2.5 g in 25 ml, is placed in a 10 cm long polarimeter cell. What will be the specific rotation if the angle of rotation is 5°.
(a) 50°
(b) 25°
(c) 125°
(d) 75°

9.57 The parachor values for hexane and heptane are 270.1 and 309.3, respectively. The parachor for the $-CH_2$ group is
(a) 39.2
(b) 6.5
(c) 78.4
(d) 5.6

9.58 The parachor values for $C_{10}H_{22}$ and CH_2 are 424.2 and 39, respectively. The parachor for the hydrogen atom is
(a) 463.2
(b) 39
(c) 34.2
(d) 17.1

9.59 If the viscosity of a saturated solution in water is 0.0100 *P* and that of pure water is 0.008 P, then the specific viscosity of the solution is
(a) 0.002
(b) 0.018
(c) 0.25
(d) 0.02

9.60 The refractive index of an organic liquid ($\rho = 1.25$ g cm^{-3} $M = 65.0$ g mol^{-1}) at 25°C is 1.5. The molar refraction is
(a) 20 cm^3 mol^{-1}
(b) 25 cm^3 mol^{-1}
(c) 31.25 cm^3 mol^{-1}
(d) 52 cm^3 mol^{-1}

Type C: True or False

9.61 The energy of molecules is greater on the surface of the liquid than in the bulk.
9.62 Due to surface tension, liquids try to have the maximum surface.
9.63 Surface active agents lower the surface tension of liquids in which they are dissolved.

9.64 The liquids which rotate plane polarised light towards the right are called dextrorotatory.

9.65 The surface tension of liquids become zero at the critical temperature.

9.66 Surface tensions of liquids decrease while viscosities increase with increase in temperature.

9.67 The compound which is optically inactive due to internal compensation is called a meso compound.

9.68 The vapour pressure of a liquid depends upon the amount of liquid taken.

9.69 The refractive index depends upon the wavelength of the light used, but independent of temperature.

9.70 According to Dunstan's rule, the value of $\frac{\rho}{M}\,\eta \times 10^6$ is below 80 for associated liquids.

Type D: Fill in the Blanks

9.71 The reciprocal of viscosity is called————.

9.72 ————is obtained by multiplying the specific refractivity by the molar mass.

9.73 The molar volume of a liquid at a temperature at which the surface tension is unity is called————.

9.74 A liquid boils at a————temperature on top of a mountain than on the sea shore.

9.75 The value of $\frac{\eta_{sp}}{C}$ obtained by extrapolating the plot of $\frac{\eta_{sp}}{C}$ vs c to zero concentration is called————.

9.76 Substances which lower the surface tension of water are called————.

9.77 Optically active compounds which rotate plane polarised light towards the right are called————, while those which rotate towards left are called————.

9.78 The specific rotation depends upon the temperature and————of light used.

9.79 Refractive index is measured in the laboratory by————.

9.80 The viscosity of a liquid————with increase in temperature.

ANSWERS

Numerical Problems

9.1 3696.8 cal mol^{-1} *9.2* 70.9°C *9.3* 1068.5 *9.4* 29.7 cm *9.5* 487.5 *9.6* 1.06 cm *9.7* 0.028 cm *9.8* 31.8% *9.9* 18.6 *9.10* 23.83 *9.11* 22.3 *9.12* 0.3465 *9.13* 0.542 cP *9.14* time (20 wt%) = 0.65 time (30 wt%) *9.15* 30.35 dm^3 *9.16* (a) 13.4 kJ (b) 1.00×10^{-2} *9.17* water is associated *9.18* 61.24 *9.19* 16.06 (acetone) *9.20* 1.369 *9.21* 26.37 *9.22* 55.8° *9.23* 5.6° *9.24* 72.4 *9.25* 164.5 mm.

Quiz Questions

9.26 (a) *9.27* (c) *9.28* (b) *9.29* (c) *9.30* (a) *9.31* (b) *9.32* (b) *9.33* (b) *9.34* (c) *9.35* (c) *9.36* (d) *9.37* (b) *9.38* (c) *9.39* (c) *9.40* (a) *9.41* (c) *9.42* (b) *9.43* (d) *9.44* (a) *9.45* (b) *9.46* (c) *9.47* (c) *9.48* (a) *9.49* (c) *9.50* (d) *9.51* (d) *9.52* (c) *9.53* (a) *9.54* (a) *9.55* (c) *9.56* (a) *9.57* (a) *9.58* (d) *9.59* (c) *9.60* (a) *9.61* True *9.62* False: Surfaces contract to have minimum surface *9.63* True *9.64* True *9.65* True *9.66* False: Surface tension and viscosity decrease with increase of temperature *9.67* True *9.68* False *9.69* True *9.70* False: The value for associated liquids is always more than 80 *9.71* fluidity *9.72* Molar refractivity *9.73* Parachor *9.74* lower *9.75* intrinsic viscosity *9.76* Surface active agents *9.77* dextrorotatory, levorotatory *9.78* wavelength *9.79* refractometer *9.80* Decreases

10

Solutions

A solution is a homogeneous mixture of two or more pure substances. Its composition can be varied within certain limits. In a solution, the component present in a lesser quantity is usually termed the solute and the component present in the larger proportion is termed the solvent. The solute and solvent, of course, can interchange roles. There are nine types of solutions possible, depending upon the physical state of the solute and solvent, but three of these, solid in liquid, liquid in liquid and gas in liquid, solutions are common and familiar.

10.1 METHODS OF EXPRESSING CONCENTRATIONS OF SOLUTIONS

The concentration of a solution may be defined as the amount of solute present in the given quantity of solution. However, the concentration of a solution for physico-chemical studies is commonly expressed in any one of the following ways:

(a) *Molarity* (M) The number of moles of solute present in one litre (1 dm^3) of solution.

(b) *Normality* (N) The number of gram equivalents of solute present in one litre (1 dm^3) of solution.

(c) *Molality* (m) The number of moles of solute present in 1000 gm (1 kg) of solvent.

(d) *Mole fraction* (x) The ratio of the number of moles of one component to the total number of moles of all components.

In addition to the above methods, the compositions of solutions can also be expressed in terms of percentage, i.e. per cent by weight, per cent by volume or mole per cent. These may be expressed as:

$$\text{Wt \% solute} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

$$\text{Vol \% solute} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

$$\text{Mole \% solute} = \frac{\text{Moles of solute}}{\text{Total moles of solution}} \times 100$$

EXAMPLE 10.1 (SI Units) Calculate the molarity and molality of a solution containing 20.7 g of potassium carbonate dissolved in 0.5 dm^3 of the given solution (assume density of solution $= 1.0 \times 10^3$ kg m^{-3}).

Solution *Calculation of molarity:*

Amount of K_2CO_3 in 0.5 dm^3 of a solution = 20.7 g

Molar mass of $K_2CO_3 = 138 \times 10^{-3}$ kg mol^{-1}

$$\text{Moles of } K_2CO_3 = \frac{20.7 \times 10^{-3} \text{ kg}}{138 \times 10^{-3} \text{ kg mol}^{-1}} = 0.15$$

Molarity = Moles of solute per dm^3 of solution

$$= \frac{0.15 \times 1}{0.5} = 0.3 \text{ M}$$

Calculation of molality:

Mass of solution $= (0.5 \times 10^{-3} \text{ m}^3) \times (1.0 \times 10^3 \text{ kg m}^{-3})$

$= 0.5$ kg $= 500$ g

Mass of water $= 500 - 20.7 = 479.3$ g $= 479.3 \times 10^{-3}$ kg

Molality = Moles of solute per kg of solvent

$$= \frac{0.15}{479.3 \times 10^{-3}} = 0.313 \text{ m}$$

EXAMPLE 10.2 A solution containing 12.6 g oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) per 500 ml had density 1.105 g ml^{-1}. Calculate (i) wt% of oxalic acid, (ii) molarity, (iii) normality, (iv) molality and (v) mole fraction of oxalic acid.

Solution (i) Wt % of oxalic acid:

12.6 g of oxalic acid present in 500 ml solution

Density of solution = 1.105 g ml^{-1}

Wt. of solution = (500 ml) × (1.105 g ml^{-1}) = 552.5 g

$$\text{Wt. \% hydrated oxalic acid} = \frac{12.6}{552.5} \times 100 = 2.28$$

(ii) Molarity:

Molecular weight of oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) = 126

$$\text{Moles of oxalic acid} = \frac{12.6}{126} = 0.1$$

Molarity = Moles of solute per litre of solution

$$= \frac{0.1}{500 \times 10^{-3}} = 0.2 \text{ M}$$

(iii) Normality:

$$\text{Equivalent weight of oxalic acid} = \frac{126}{2} = 63$$

$$\text{Gram equivalents of oxalic acid} = \frac{12.6}{63} = 0.2$$

Normality = gram equivalent of solute per litre of solution

$$= \frac{0.2}{500 \times 10^{-3}} = 0.4 \text{ N}$$

(iv) Molality:

Wt. of solution = 552.5 g

Wt. of water present = 552.5 − 12.6 = 539.9 g

Molality = g mol of solute per kg of solvent

$$= \frac{0.1}{539.9 \times 10^{-3}} = 0.185 \text{ m}$$

(v) Mole fraction of oxalic acid:

Moles of oxalic acid = 0.1

$$\text{Moles of water} = \frac{539.9}{18} = 30$$

$$\text{Mole fraction } (x) = \frac{\text{Moles of oxalic acid}}{\text{Total moles of solution}}$$

$$= \frac{0.1}{0.1+30} = 0.00033$$

10.2 RAOULT'S LAW

According to Raoult's law the partial pressure of any volatile component of a solution at a given temperature is equal to the vapour pressure of the pure component multiplied by its mole fraction.

i.e., $$p_i = x_i \, p_i^\circ \tag{10.1}$$

where p_i is the vapour pressure of the component i over the solution, x_i is its mole fraction, and p_i° is the vapour pressure of the pure component at the same temperature.

In a binary solution containing x_1 and x_2 mole fractions of two components having p_1^0 and p_2^0 vapour pressures in their pure states, the partial vapour pressures p_1 and p_2 are

$$p_1 = p_1^0 \, x_1$$

and $$p_2 = p_2^0 \, x_2$$

The total pressure above the solution is

$$p = p_1 + p_2 = p_1^0 \, x_1 + p_2^0 (1 - x_1) = (p_1^0 - p_2^0) \, x_1 + p_2^0$$

The activity of a component obeying Raoult's law is equal to its mole fraction.

10.3 IDEAL SOLUTIONS AND THERMODYNAMIC PROPERTIES OF SOLUTIONS

Solutions in which the components obey Raoult's law over the entire composition range are said to be ideal solutions. For an ideal solution, the change in Gibbs free energy is given by

$$\Delta G_{\text{mix}} = G_{\text{solution}} - G_{\text{pure components}}$$

If the solution is formed by n_1 moles of component 1 and n_2 moles of component 2, then

$$\Delta G_{\text{mix}} = n_1\, RT \ln x_1 + n_2\, RT \ln x_2 \tag{10.2}$$

From this, other thermodynamic properties can be obtained:

$$\text{Entropy of mixing, } \Delta S_{\text{mix}} = \frac{\delta \Delta G_{\text{mix}}}{\delta T} = -R[n_1 \ln x_1 + n_2 \ln x_2] \tag{10.3}$$

$$\text{Enthalpy of mixing, } \Delta H_{\text{mix}} = T^2 \frac{\partial(\Delta G_{\text{mix}}/T)}{\partial T} = 0 \tag{10.4}$$

$$\text{Volume of mixing, } \Delta V_{\text{mix}} = \frac{\partial(\Delta G_{\text{mix}})}{\partial p} = 0 \tag{10.5}$$

Equations (10.2) to (10.5) give the thermodynamic functions of mixing for solutions. From these, the changes per mole can also be calculated, e.g. Gibbs free energy of mixing per mole is given by

$$\begin{aligned}\frac{\Delta G_{\text{mix}}}{n_1+n_2} = \Delta G_{m(\text{mix})} &= \frac{n_1}{n_1+n_2} RT \ln x_1 + \frac{n_2}{n_1+n_2} RT \ln x_2 \\ &= x_1\, RT \ln x_1 + x_2\, RT \ln x_2 \\ &= RT\,[x_1 \ln x_1 + x_2 \ln x_2] \qquad (10.6)\end{aligned}$$

Similarly, $\Delta S_{m(\text{mix})} = -R[x_1 \ln x_1 + x_2 \ln x_2]$ (10.7)

$\Delta H_{m(\text{mix})} = 0, \quad \Delta V_{m(\text{mix})} = 0$ (10.8)

Thus, thermodynamically, ideal solutions are those in which there is no enthalpy or volume change upon mixing the components.

Physically, this is possible only if molecules of the two components are of the same size and have exactly the same interactions as between molecules of each pure component.

EXAMPLE 10.3 The vapour pressure of methyl alcohol at 25°C is 90 torr. Its mole fraction in a solution with ethyl alcohol is 0.204. What is its vapour pressure if it obeys Raoult's law?

Solution According to Raoult's law,

$$p_1 = p_1^\circ\, x_1$$

Vap. pressure of pure methyl alcohol, $p_1^\circ = 90$ torr

Mole fraction of methyl alcohol, $x_1 = 0.204$

Vap. pressure of methyl alcohol in solution,

$$p_1 = 90 \times 0.204 = 18.36 \text{ torr.}$$

EXAMPLE 10.4 (SI Units) Calculate the vapour pressure over a solution containing 1 mol of benzene and 2.5 mol of toluene at 320 K, if the vapour pressures of pure components at this temperature are 3.2×10^4 N m^{-2} and 1.02×10^4 N m^{-2}, respectively (assume solution obeying Raoult's law).

Solution Number of moles of benzene $(n_1) = 1$

Number of moles of toluene $(n_2) = 2.5$

$$\text{Mole fraction of benzene, } x_1 = \frac{n_1}{n_1+n_2} = \frac{1}{1+2.5} = 0.29$$

$$\text{Mole fraction of toluene, } x_2 = \frac{2.5}{1+2.5} = 0.71$$

Applying Raoult's law,

$$p_1 = p_1^\circ \times x_1$$

where $p_1^\circ = 3.2\times10^4$ N m^{-2}

$$p_1 = 3.2\times10^4\times0.29 = 0.928\times10^4 \text{ N m}^{-2}$$

$$p_2 = p_2^\circ \times x_2$$

where $p_2^\circ = 1.02\times10^4$ N m^{-2}

$$p_2 = 1.02\times10^4\times0.71 = 0.724\times10^4 \text{ N m}^{-2}$$

Thus, total pressure $p = p_1+p_2$

$$= 0.928\times10^4+0.724\times10^4$$

$$= 1.652\times10^4 \text{ N m}^{-2}$$

EXAMPLE 10.5 The vapour pressures of pure n-hexane and n-heptane at 50°C are 406.5 torr and 140 torr, respectively. Assuming a solution of these substances obeys Raoult's law, determine the composition of vapour in equilibrium with a solution containing 20 mol % of n-hexane at this temperature.

Solution

Mole fraction of n-hexane, $x_1 = 0.20$

Mole fraction of n-heptane, $x_2 = 0.80$

Vapour pressures at 30°C

$$p_1^\circ = 406.5 \text{ torr}, \ p_2^\circ = 140 \text{ torr}$$

Now, $p_1 = p_1^\circ\, x_1 = 406.5\times0.20 = 81.3$ torr

$$p_2 = p_2^\circ\, x_2 = 140\times0.80 = 112 \text{ torr}$$

Total pressure, $p = p_1+p_2 = 81.3+112 = 193.3$ torr

The composition of the vapour phase can be calculated as,

Mole fraction of n-hexane, $y_1 = \dfrac{p_1}{p}$

$$= \frac{81.3}{193.3} = 0.42$$

Mole fraction of n-heptane, $y_2 = 1-y_1$

$$= 1-0.42 = 0.58$$

EXAMPLE 10.6 At 27°C, one mole of m-xylene is mixed with three moles of p-xylene to form an ideal solution. Calculate the Gibbs free energy, entropy and enthalpy of mixing per mole.

Solution The free energy of mixing per mole,

$$\Delta G_{m(\text{mix})} = RT\,[x_1 \ln x_1+x_2 \ln x_2]$$

Number of moles of m-xylene, $n_1 = 1$

Number of moles of p-xylene, $n_2 = 3$

Mole fraction, $x_1 = \dfrac{n_1}{n_1+n_2} = \dfrac{1}{1+3} = 0.25$

$$x_2 = \frac{n_2}{n_1+n_2} = \frac{3}{1+3} = 0.75$$

$$R = 1.98 \text{ cal K}^{-1}\text{ mol}^{-1}, \ T = 27+273 = 300 \text{ K}$$

$$\Delta G_{m(\mathrm{mix})} = 1.98\times 300\times 2.303 \quad [0.25 \log 0.25+0.75 \log 0.75]$$
$$= -334.1 \text{ cal mol}^{-1}$$

Entropy of mixing per mole

$$\Delta S_{m(\mathrm{mix})} = -R\,[x_1 \ln x_1+x_2 \ln x_2]$$
$$=-1.98\times 2.303\ [0.25 \log 0.25+0.75 \log 0.75]$$
$$= 1.1 \text{ cal K}^{-1}\text{ mol}^{-1}$$

Enthalpy of mixing per mole,

$$\Delta H_{m(\mathrm{mix})} = 0 \quad \text{(for ideal solution)}$$

10.4 REAL SOLUTIONS

Real solutions deviate from ideal solutions. For real solutions, the Gibbs free energy change of mixing is given by

$$\Delta G_{(\mathrm{mix})} = RT\,[n_1 \ln a_1+n_2 \ln a_2]$$
$$= RT\,[n_1 \ln x_1\gamma_1+n_2 \ln x_2\gamma_2] \qquad (10.9)$$

or

$$\Delta G_{m(\mathrm{mix})} = RT\,[x_1 \ln a_1+x_2 \ln a_2]$$
$$= RT\,[x_1 \ln x_1\gamma_1+x_2 \ln x_2\gamma_2] \qquad (10.10)$$

where γ_1 and γ_2 are the activity coefficients of components 1 and 2.

The difference between the Gibbs free energy of mixing for real solutions and ideal solutions is called the *excess Gibbs free energy of mixing*, i.e.

$$\Delta G^E_m = \Delta G_{m(\mathrm{real})}-\Delta G_{m(\mathrm{ideal})}$$

$$\Delta G_m{}^E= RT[x_1 \ln x_1\gamma_1+x_2 \ln x_2\gamma_2]$$
$$- RT[x_1 \ln x_1+x_2 \ln x_2] \qquad (10.11)$$
$$= RT[x_1 \ln \gamma_1+x_2 \ln \gamma_2]$$

Similarly, it can be shown that

$$\Delta S^E_m = -RT\left[x_1\left(\frac{\partial \ln \gamma_1}{\partial T}\right)_p+x_2\left(\frac{\partial \ln \gamma_2}{\partial T}\right)_p\right]-R\,[x_1 \ln x_1+x_2 \ln x_2] \qquad (10.12)$$

$$\Delta H^E_m = -RT^2\left[x_1\left(\frac{\partial \ln \gamma_1}{\partial T}\right)_p+x_2\left(\frac{\partial \ln \gamma_2}{\partial T}\right)_p\right] \qquad (10.13)$$

At low pressures, fugacity can be equated to vapour pressure. Hence,

$$\frac{f_1}{f_1^\circ} = \frac{p_1}{p_1^\circ} = a_1 = \gamma_1 x_1$$

or

$$p_1 = p_1^\circ\ \gamma_1\ x_1$$

Depending upon the value of γ_i's, the partial pressure of the component may be greater or lesser than the Raoult's law pressure. If $\gamma_i>1$, the system shows positive deviations from Raoult's law and if $\gamma_i<1$, it shows negative deviations. As a result, solutions may be divided into three types.

Type I Solutions show small deviations from ideal behaviour. Total pressure is always within the vapour pressures of the pure components.

Type II Solutions show positive deviations and a maximum in the total vapour pressure curve.

Type III Solutions show negative deviations and a minimum in the total vapour pressure curve.

The vapour pressure-liquid composition curves for the three types are shown in Figs. 10.1 (a), (b) and (c). It is clear from the figures that the vapour composition curves lie below the liquid-composition curves for all types. In the systems of Types II and III [Fig. 10.1 (b) and (c)], the two curves are in contact at the points of maximum and minimum vapour pressure, respectively.

The separation of two components in a solution by distillation is based upon the principle that the composition of the vapour phase is different from that of the liquid phase. The boiling point is the temperature at which the total vapour pressure becomes equal to the confining pressure (atmosphere pressure). Since different compositions of a solution have different vapour pressures, solutions of various concentrations will boil at different temperatures. Obviously, a solution of low

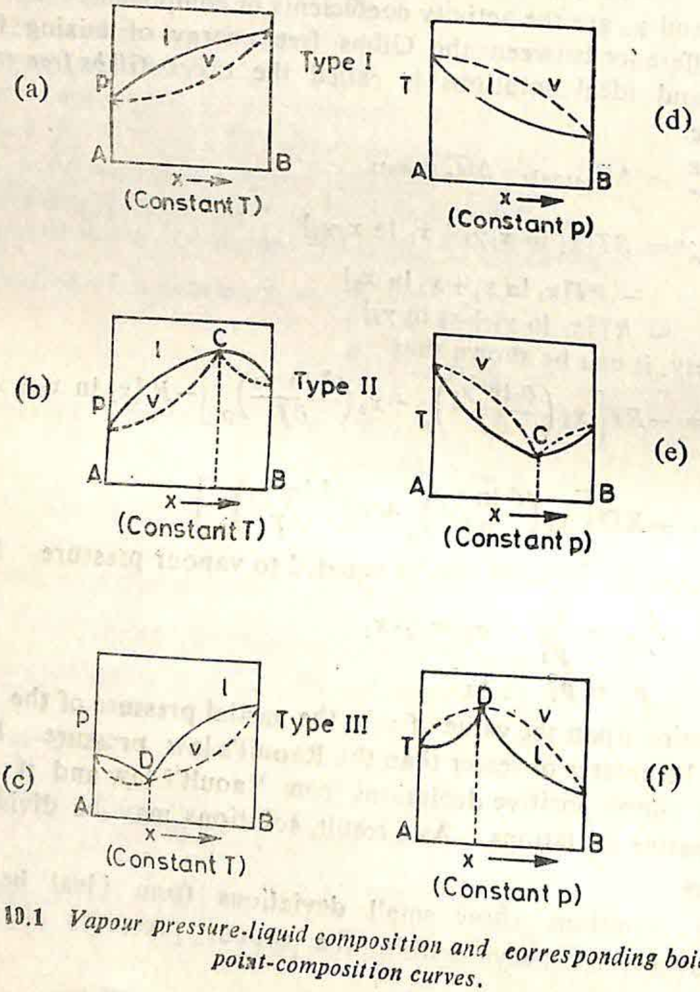


Fig. 10.1 *Vapour pressure-liquid composition and corresponding boiling point-composition curves.*

vapour pressure will boil at a higher temperature than one of higher vapour pressure. The boiling point composition curves are also given in Fig. 10.1 [(d), (e) and (f)].

According to Fig. 10.1, it is possible to isolate the pure components by repeated fractional distillation.

It may be noted that,

(a) The two components forming a solution of Type I can be separated by fractional distillation into the pure components.

(b) The fractional distillation of a solution of Type II gives residues of A and B and a distillate of composition C. For example, the distillation of a solution of composition between A and C will give a residue of A and a final distillate of composition C. The distillation of a solution of composition between B and C will give a residue of B and distillate of composition C.

(c) In the fractional distillation of a solution of Type III, the residues tend towards a boiling mixture and the distillates towards the pure components.

Mixtures which boil at constant temperatures are called constant *boiling mixtures* or *azeotropes*. Their composition in the liquid and vapour phase is the same.

10.5 SOLUBILITY OF PARTIALLY MISCIBLE LIQUIDS

There are certain liquids which are only partially miscible with one another. The miscibility of these solutions varies with temperature in a characteristic manner. At the compositions when they are not completely miscible, two liquid layers are formed. For example, in the case of aniline and water, one layer consists of a small amount of water dissolved in aniline while the other layer consists of a small amount of aniline dissolved in water. Such solutions of different compositions coexisting with one another are called *conjugate solutions*.

In these solutions, the mutual miscibility varies with temperature so that, at a certain temperature, the two layers become completely miscible. This temperature is known as the *critical temperature* or *consolute tempesature*. Systems in which mutual solubility increases with temperature have upper *consolute* temperatures (e.g. aniline+water), while those in which mutual solubility increases with decrease in temperature possess lower consolute temperature (e.g. triethylamine and water). There are solutions which show upper as well as lower consolute temperatures (e.g. nicotine and water).

10.6 STEAM DISTILLATION

This technique is generally used for the purification of organic liquids which either boil at higher temperatures or decompose when boiled at atmospheric pressure. In this type of distillation of liquids immiscible with water, the distillate separates in two layers consisting of water and organic liquid. The total pressure due to organic liquid and water vapour is equal to the atmospheric pressure. The ratio of components '1' and '2' in the vapour phase, which distil over (distillate), is given by

$$\frac{w_1}{w_2} = \frac{p_1^\circ M_1}{p_2^\circ M_2} \qquad (10.14)$$

where w_1, w_2 are the weights, p_1°, p_2° are vapour pressures and M_1, M_2 are the molar masses of components '1' and '2', respectively.

EXAMPLE 10.7 In a solution of water and alcohol, the mole fraction of water is 0.5. The partial pressures of water and alcohol over the solution are 13.5 and 27.6 torr, respectively. The vapour pressures of pure water and alcohol at this temperature of the solution are 17.5 and 43.6 torr, respectively. Calculate

(a) activities of water and alcohol
(b) activity coefficients of water and alcohol.

Solution (a) Activity, $a = \frac{p}{p^\circ}$

$$a_{(H_2O)} = \frac{p_{(H_2O)}}{p^\circ_{(H_2O)}}$$

$$p_{(H_2O)} = 13.5 \text{ torr}, \quad p^\circ_{(H_2O)} = 17.5 \text{ torr}$$

$$a_{(H_2O)} = \frac{13.5}{17.5} = 0.77$$

$$a_{(C_2H_5OH)} = \frac{p_{(C_2H_5OH)}}{p^\circ_{(C_2H_5OH)}}$$

$$p_{(C_2H_5OH)} = 27.6 \text{ torr}, \quad p^\circ_{(C_2H_5OH)} = 43.6 \text{ torr}$$

$$a_{(C_2H_5OH)} = \frac{27.6}{43.6} = 0{,}63$$

(b) Activity coefficient $\gamma = \frac{a}{x}$

$$\gamma_{(H_2O)} = \frac{a_{(H_2O)}}{x_{(H_2O)}} \qquad a_{(H_2O)} = 0.77$$

$$x_{(H_2O)} = 0.5$$

$$\gamma_{(H_2O)} = \frac{0.77}{0.5} = 1.54$$

$$\gamma_{(C_2H_5OH)} = \frac{a_{(C_2H_5OH)}}{x_{(C_2H_5OH)}}$$

$$a_{(C_2H_5OH)} = 0.63, \quad x_{(C_2H_5OH)} = 0.5$$

$$\gamma_{(C_2H_5OH)} = \frac{0.63}{0.5} = 1.26$$

EXAMPLE 10 8 A certain mixture of water and chlorobenzene boiled at 90°C under a reduced pressure of 720 torr. If the vapour pressure of water at 90°C is 528 torr, calculate the composition of the distillate on wt% basis.

Solution The ratio of components of the distillate is

$$\frac{w_1}{w_2} = \frac{p_1^\circ M_1}{p_2^\circ M_2}$$

Wt. of water $= w_1$
Wt. of chlorobenzene $= w_2$
Vap. pressure of water, $p_1^\circ = 528$ torr

Vap. pressure of chlorobenzene, $p_2^\circ = 720 - 528 = 192$ torr
Molar mass of water, $M_1 = 18$
Molar mass of chlorobenzene $= 112.5$

$$\frac{w_1}{w_2} = \frac{528 \times 18}{192 \times 112.5} = 0.44$$

If the weight of chlorobenzene in distillate w_2 is 1, then the weight of water in distillate is 0.44. This means that 1.44 parts of mixture contain 1 part of chlorobenzene.

$$\text{Wt \% of chlorobenzene} = \frac{1}{1.44} \times 100 = 69.4\%$$

$$\text{Wt \% of water} = 100 - 69.4 = 30.6\%$$

EXAMPLE 10.9 A mixture of immiscible liquids of an organic liquid and water boils at 90°C and 732 torr pressure. The distillate contains 73% by weight of the organic liquid. Calculate the molar mass of the organic liquid (vapour pressure of water at 90°C is 526 torr).

Solution The ratio of components of the distillate is

$$\frac{w_1}{w_2} = \frac{p_1^\circ M_1}{p_2^\circ M_2}$$

Wt. of water, $w_1 = 27$ g
Wt. of organic liquid, $w_2 = 73$ g
Total vapour pressure at 90°C = 732 torr

Vap. pressure of water, $p_1^\circ = 526$ torr

Vap. pressure of organic liquid, $p_2^\circ = 732 - 526 = 206$ torr

Molar mass of water, $M_1 = 18$

Molar mass of organic liquid, $M_2 = ?$

$$M_2 = \frac{p_1^\circ\, M_1\, w_2}{p_2^\circ\, w_1}$$

$$= \frac{(526 \text{ torr}) \times (18 \text{ g mol}^{-1}) \times (73 \text{ g})}{(206 \text{ torr}) \times (27 \text{ g})}$$

$$= 124.2 \text{ g mol}^{-1}$$

10.7 SOLUBILITY OF A GAS IN A LIQUID

The solubility of a gas in a liquid at a given temperature depends upon the nature of the gas and the solvent. The most soluble gases are those which react with the liquid chemically. The solubility of a gas decreases with temperature and increases with increase of pressure over the solution at a given temperature.

The solubility of a gas is related to its pressure by Henry's law. This states that the mass of dissolved gas per unit volume of solvent, at a given temperature, is proportional to the pressure of the gas in equilibrium with the solution.

If x is the mole fraction of gas in the solvent and p is the gas pressure in equilibrium with the solution, then

$$x \propto p$$

or $$x = K'p$$

or $$p = K\,x$$

where K is called Henry's constant (10.15)

The units of K will depend upon the units of pressure and the concentration. If the concentration is expressed in units other than mole fraction, then the units of the Henry's law constant will change accordingly.

It has been observed that Henry's law is valid if

(i) pressure is not too high

(ii) temperature is not too low and

(iii) the gas is not highly soluble and does not dissociate or interact strongly or chemically with the solvent.

10.8 HENRY'S AND RAOULT'S LAWS

According to Henry's law,

$$p = K\,x$$

i.e. pressure is directly proportional to mole fraction. But Raoult's law states that

$$p = p^\circ x$$

$$\therefore \quad K = p^\circ$$

This means that Raoult's law is a special case of Henry's law. It may be noted that:

(a) If one component obeys Raoult's law over a certain range of compositions, the other component must obey Henry's law in that composition range.

(b) If one component obeys Raoult's law over the entire range of compositions, then the other component must also obey Raoult's law and the solution is ideal.

EXAMPLE 10.10 One litre of water under a nitrogen pressure of 1 atm dissolves 0.02 g of nitrogen at 20°C. Calculate Henry's law constant.

Solution According to Henry's law,

$$p = K\,x$$

$$x = \frac{\text{Moles of nitrogen}}{\text{Moles of nitrogen} + \text{Moles of water}}$$

$$= \frac{0.02/28}{0.02/28 + 1000/18} = 1.129 \times 10^{-5}$$

$$p = 1 \text{ atm}$$

$$K = \frac{p}{x} = \frac{1 \text{ atm}}{1.29 \times 10^{-5}} = 7.75 \times 10^4 \text{ atm}$$

EXAMPLE 10.11 Dry air contains 79% N_2 and 21% O_2. Determine the proportion of N_2 and O_2 dissolved in water at 1 atm pressure. Henry's constants for N_2 and O_2 in H_2O are 8.54×10^4 atm and 4.56×10^4 atm, respectively.

Solution The total pressure of air over water is 1 atm. The partial pressures of N_2 and O_2 are

$$p_{(N_2)} = \frac{1 \times 79}{100} = 0.79 \text{ atm}$$

$$p_{(O_2)} = \frac{1 \times 21}{100} = 0.21 \text{ atm}$$

Applying Henry's law,

$$p_{(N_2)} = K_{(N_2)} \cdot x_{(N_2)}$$

or

$$x_{(N_2)} = \frac{p_{(N_2)}}{K_{(N_2)}} = \frac{0.78}{8\ 54 \times 10^4} = 9.13 \times 10^{-6}$$

Similarly, $$x_{(O_2)} = \frac{p_{(O_2)}}{K_{(O_2)}} = \frac{0.21}{4.56 \times 10^4} = 4.60 \times 10^{-6}$$

$\therefore$ proportion of $N_2/O_2 = 1.98 : 1$

10.9 NERNST DISTRIBUTION LAW

If a solute is dissolved in two immiscible or sparingly soluble liquids, and has the same molecular state in both these liquids, then the ratio of the concentration of the solute in the two phases at equilibrium is constant, i.e.

$$\frac{C_1}{C_2} = K \tag{10.16}$$

where C_1 is the concentration of the solute in phase 1 and C_2 is the concentration in phase 2. K is called the distribution or partition coefficient. This is known as the *Nernst distribution law*. If the solutions in the two solvents are non-ideal, then the concentrations are replaced by their activities, i.e. $a_1/a_2 = K$.

When the molecular state of the solute is different (association or dissociation) in one of the phases, the distribution law is modified as:

(a) *Association of the solute in one of the phases* Suppose a solute 'S' remains as such in the first phase and exists as both 'S' and its associated form 'S_n' but predominantly as S_n in second phase, Then

$$K = \frac{C_1}{[C_2]^{1/n}} \tag{10.17}$$

where n is called the degree of association. If the value of n is unknown, then it can be determined from the equation,

$$\log C_1 = \frac{1}{n} \log C_2 + \log K$$

by plotting a graph between $\log C_2$ and $\log C_1$ so that the slope is equal to $1/n$.

(b) *Dissociation of the solute in one of the phases* When a solute 'HS' exists as such in phase 1 and exists both as 'HS' and its dissociated form ($HS \rightleftharpoons H + S$) in phase 2, then

$$K = \frac{C_1}{C_2(1-\alpha)} \tag{10.18}$$

where α is the degree of dissociation.

(c) *Solute forms complex in one of its phases* The combination of the solute with some other species in one of the phases does not make any change in the distribution law equation, but it changes its numerical value.

Distribution Law and Solvent Extraction

Organic compounds generally have higher solubilities in organic solvents than in water. They are generally extracted from aqueous solutions by shaking repeatedly with organic solvents. It can be shown that the process of extraction will be more economical if the extracting liquid is used in several instalments instead of all at once. If a grams of solute are present in V ml of water, and is shaken with v ml of organic liquid, then the weight of solute left after the nth extraction, w_n is

$$w_n = a\left(\frac{kV}{kV+v}\right)^n \tag{10.19}$$

The weight of solute extracted will be

$$a - w_n = a\left[1 - \left(\frac{kV}{kV+v}\right)^n\right] \tag{10.20}$$

where K is the distribution coefficient.

EXAMPLE 10.12 Distribution of benzoic acid has been studied between water and benzene. The concentrations of benzoic acid determined by titration are given below:

$C(C_6H_6)$ mol l^{-1}	0.1302	0.0982	0.0501
$C(H_2O)$ mol l^{-1}	0.0100	0.0087	0.0062

Determine the nature of association of benzoic acid in benzene.

Solution

$C(C_6H_6)$ mol l^{-1}	$C(H_2O)$ mol l^{-1}	$\frac{C(H_2O)}{C(C_6H_6)}$	$\frac{C(H_2O)}{[C(C_6H_6)]^{1/2}}$ mol$^{1/2}$ $l^{-1/2}$
0.1302	0.0100	0.077	0.0277
0.0982	0.0087	0.089	0.0278
0.0501	0.0062	0.124	0.0277

It is clear that $C(H_2O)/C(C_6H_6)$ is not constant and, therefore, benzoic acid does not exist in the same molecular state in two phases. But $C(H_2O)/[C(C_6H_6)]^{1/2}$ is almost constant. Thus, the degree of association of benzoic acid in benzene is two, i.e. it exists as a dimer in benzene.

EXAMPLE 10.13 The distribution coefficient of I_2 between CCl_4 and H_2O is 85. When iodine is shaken with CCl_4 and 0.05 M potassium iodide solution, the concentration of iodine in CCl_4 and aqueous layers are 0.05 and 0.015 M. Calculate the equilibrium constant for the reaction:

$$I_2 + I^- \rightleftharpoons I_3^- \quad \text{in aqueous layer}$$

Solution Concentration of I_2 in CCl_4 layer,

$$[I_2(CCl_4)] = 0.05 \text{ M}$$

$$K = \frac{[I_2(CCl_4)]}{[I_2(H_2O)]} = 85$$

$$[I_2(H_2O)] = \frac{0.05}{85} = 5.88 \times 10^{-4} \text{ M}$$

$$[I_3^-(H_2O)] = C(H_2O) - [I_2(H_2O)]$$

$$= 0.015 - 5.88 \times 10^{-4}$$

$$= 0.01441 \text{ M}$$

$$[I^-(H_2O)] = 0.05 - 0.01441 = 0.03559 \text{ M}$$

Hence, for the reaction

$$I_2 + I^- \rightleftharpoons I_3^-$$

$$K_{eq} = \frac{[I_3^-(H_2O)]}{[I_2(H_2O)][I^-(H_2O)]}$$

$$= \frac{0.01441}{(0.000588) \times (0.03559)} = 688.6 \text{ M}^{-1}$$

Example 10.14 One litre of an aqueous solution, on shaking twice with 50 ml of an organic liquid, retains 3.46 g of solute. Initially, the amount of solute in the solution was 5 g. What is the distribution coefficient of solute between water and ether (assume the same molecular state for the solute in both solvents) ?

Solution

Weight of solute remaining unextracted,

$$w_n = a\left(\frac{KV}{KV + v}\right)^n$$

$w_n = 3.46$ g, $a = 5.0$ g, $V = 1000$ ml, $v = 50$ ml, $n = 2$

$$3.46 = 5.0\left(\frac{K \times 1000}{K \times 1000 + 50}\right)^2$$

or $$\frac{1000\,K}{1000\,K + 50} = \left(\frac{3.46}{5.0}\right)^{\frac{1}{2}} = 0.832$$

or $$K = 0.248$$

Example 10.15 One gram of a substance is present in 100 ml of water. The solution is shaken with chloroform, using 50 ml of chloroform at a time, in two instalments.

(a) Calculate the amount of substance left unextracted if the distribution coefficient of the substance between chloroform and water is 5:1. Assume the same molecular state for the solute in both solvents.

(b) Show that the amount extracted in two instalments is more than when using 100 ml at a time.

Solution (a) Amount of substance left unextracted after two operations,

$$w_n = a\left(\frac{KV}{KV + v}\right)^2$$

$a = 1$ g, $V = 100$ ml, $v = 50$ ml, $n = 2$, $K = 1/5$

$$\therefore \quad w_2 = 1\left(\frac{1/5 \times 100}{1/5 \times 100 + 50}\right)^2$$

$$= 0.082 \text{ g}$$

(b) Amount of substance extracted in two instalments = 1 − 0.082

$$= 0.918 \text{ g}$$

If 100 ml is used in one operation, then the amount of substance left unextracted,

$$w_1 = a\left(\frac{KV}{KV + v}\right)$$

$$a = 1 \text{ g}, \quad K = 1/5, \quad V = 100 \text{ ml}, \quad v = 100 \text{ ml}$$

$$w_1 = 1\left(\frac{1/5 \times 100}{1/5 \times 100 + 100}\right)$$

$$= 0.167 \text{ g}$$

Amount of substance extracted in one operation $= 1 - 0.167 = 0.833$ g

Hence, amount of solute extracted in two instalments is more than that extracted in one instalment.

MISCELLANEOUS EXAMPLES

EXAMPLE 10.16 At 25°C, two moles of cyclohexane are mixed with three moles of iso-octane. The activity coefficients of cyclohexane and iso-octane in the solution are found to be 1.049 and 0.996, respectively. Calculate the Gibbs free energy change of mixing per mole of the mixture. By how much is it greater than the corresponding value in an ideal solution of the same composition?

Solution Gibbs free energy change of mixing per mole

$$\Delta G_{m(\text{mix})} = RT[x_1 \ln a_1 + x_2 \ln a_2]$$

$$= RT[x_1 \ln x_1\gamma_1 + x_2 \ln x_2\gamma_2]$$

$R = 1.98$ cal, $\quad T = 273 + 25 = 298$ K

Moles of cyclohexane, $n_1 = 2$, Moles of iso-octane, $n_2 = 3$

Mole fractions, $x_1 = \dfrac{2}{2+3} = 0.4$, $x_2 = \dfrac{3}{2+5} = 0.6$

Activity coefficients, $\quad \gamma_1 = 1.049, \quad \gamma_2 = 0.996$

$$\Delta G_{m(\text{mix})} = 1.98 \times 298 \times 2.303 \quad [0.4 \log (0.4 \times 1.049) + 0.6 \log (0.6 \times 0.996]$$

$$= -387.4 \text{ cal mol}^{-1}$$

For ideal solutions

$$\Delta G_{m(\text{mix})} = RT[x_1 \ln x_1 + x_2 \ln x_2]$$

$$= 1.98 \times 298 \times 2.303 \quad [0.4 \log (0.4) + 0.6 \log (0.6)]$$

$$= -397.1 \text{ cal mol}^{-1}$$

Difference of non-ideal and ideal (excess Gibbs free energy change)

$$\Delta G^{E}_{m(\text{mix})} = -(387.4) - (-397.1) = 9.7 \text{ cal mol}^{-1}$$

EXAMPLE 10.17 A solution contains 1 g of an organic compound in 500 ml of aqueous solution. It can be extracted with ether. Calculate the minimum number of extractions needed for at least 90% recovery of the compound, using 25 ml ether each time. The distribution coefficient of the compound between ether/water is 20.

Solution The amount of compound left after the *n*th extraction is

$$w_n = a\left(\frac{KV}{KV + v}\right)^n$$

Distribution coefficient, $K = \dfrac{C(H_2O)}{C(\text{ether})} = \dfrac{1}{20}$

$a = 1$ g, $V = 500$ ml, $v = 25$ ml, $w_n = 100 - 90 = 10\%$ or $\dfrac{10}{100}$

$$\frac{10}{100} = 1\left(\frac{\frac{1}{20} \times 500}{\frac{1}{20} \times 500 + 20}\right)^n$$

$$\frac{1}{10} = \left(\frac{25}{45}\right)^n$$

Taking logs,

$$\log\left(\frac{1}{10}\right) = n \log\left(\frac{25}{45}\right)$$

or
$$n = \frac{\log\left(\frac{1}{10}\right)}{\log\left(\frac{25}{45}\right)} = 3.91$$

Thus, *four extractions* are required to get 90% recovery.

QUESTIONS

Numerical Problems

10.1 (SI Units) Calculate the molarity and molality of a solution containing 30 g of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) dissolved in 1 dm^3 of solution. The density of the solution is 1.0×10^3 kg m^{-3}.

10.2 Calculate the molarity and molality of a sulphuric acid solution containing 30% H_2SO_4 by weight (density of solution = 1.198 g cm^{-3}).

10.3 Calculate the molality and mole fraction of solute in a solution made by dissolving 18 g of glucose (molar mass = 180) in 500 g of water.

10.4 What will be the molarity of a solution prepared by mixing 3 *l* of 0.1 M HCl with 2 *l* of 5 M HCl ?

10.5 5 g of tetramethylammonium chloride $(CH_3)_4NCl$, has been dissolved in 600 g of ethanol. Express the concentration in molarity, molality, mole fraction and percentage by weight (density of the solution is 0.8025 g cm^{-3}).

10.6 How much NaOH containing 50% water by weight is required to prepare 2 *l* of 0.1N NaOH solution ?

10.7 (SI Units) At 300 K, the vapour pressures of toluene and benzene are 3.572 kPa and 9.657 kPa, respectively. Assuming nearly ideal solution of toluene and benzene, calculate

(a) the vapour pressure of a solution containing 0.4 mol fraction of toluene

(b) the mole fraction of toluene in the vapour over the solution

10.8 The vapour pressures of pure components *A* and *B* are 120 torr and 96 torr, respectively. What will be the partial pressures of the components and the total pressure when the solution contains 1 mole of component *A* and 4 moles of component *B* and the solution is ideal? What will be the composition in the vapour phase?

10.9 (SI Units) At 323 K, the vapour pressures of pure chloroform and acetone are 98.6 kPa and 84.0 kPa. In a solution of chloroform and acetone, the mole fraction of acetone is 0.4 and the vapour pressure of chloroform and acetone over the solution are 53.3 kPa and 26.6 kPa, respectively. Calculate the activities and activity coefficients of the components.

10.10 At 25°C, 1 mole of $SiCl_4$ and 3 moles of n-heptane are mixed to give a solution in which the activity coefficients are 1.15 and 1.01, respectively. Calculate the Gibbs free energy of mixing per mole. By how much is it greater than the corresponding value in an ideal solution of the same composition?

10.11 (SI Units) Calculate ΔG_m^E when 3 moles of cyclohexane are mixed with 1 mole of ethyl benzene at 313 K. The activity coefficients of cyclohexane and ethyl benzene are 1.038 and 1.175, respectively.

10.12 (a) During steam distillation of a mixture of chlorobenzene and water, the mixture boils at 95°C and 750.6 torr pressure. Calculate the composition of the distillate (vap. pressure of water at 95°C = 634.6 torr).

(b) A mixture of an organic liquid and water boils at 90°C and 733.5 torr. The distillate contains 30% by weight of the organic liquid. Calculate the molar mass and vapour pressure of the organic liquid (vapour pressure of water at 90°C is 526 torr).

10.13 (SI Units) The vapour pressures of pure benzene and toluene at 293 K are 1.01×10^4 N m^{-2} and 2.92×10^3 N m^{-2}, respectively. Calculate the composition of vapour in equilibrium with the solution containing 25 mol % benzene, assuming the solution to obey Raoult's law.

10.14 The Henry's law constant for krypton in water is 2×10^4 atm^{-1} at 20°C. How many grams of Kr should dissolve in 2000 g of water at a krypton pressure of 15 atm at this temperature (at mass of krypton = 83.8)?

10.15 How many grams of oxygen will be adsorbed by 10 *l* of water at 25°C, when the pressure of oxygen over water in equilibrium is 2 atm? Henry's law constant is 4.22×10^5 torr.

10.16 The mole fraction of acetone in dilute aqueous solution is 0.0333, and it i known to obey Henry's law for acetone. The partial pressure of acetone over this solution is 38 torr.

(a) Determine the Henry's law constant.

(b) What will be the partial pressure of acetone on the basis of Henry's law if its mole fraction is 0.0666?

10.17 The vapour pressures of pure *A* and *B* are 300 and 400 torr, respectively, at 27°C. The components *A* and *B* form a non-ideal solution, but the vapour phase above the solution behaves ideally. The total pressure above the solution that is 50 mole % *A* is found to be 250 torr and the mole fraction of *A* in the vapour phase is 0.40. Calculate the activities and activity coefficients of *A* and *B* in the solution.

10.18 The distribution constant of ammonia between water and chloroform is 27.5. Two hundred ml of a 0.01 molar solution of ammonia in chloroform is shaken with 20 ml of water. What will be the number of moles of ammonia left in the chloroform layer after equilibrium?

10.19 Acetic acid was shaken with CCl_4 and H_2O. On analysis of two layers, the following results were obtained:

Conc. in H_2O	5.00	7.38	12.86
Conc. in CCl_4	0.30	0.65	1.98

Assuming that acetic acid exists as a single molecule in water, show that it exists as a dimer in CCl_4.

10.20 The solubilities of iodine in water and carbon disulphide, at 25°C are 0.030 g and 20 g per 100 ml, respectively. One litre of a saturated solution of iodine is shaken with 10 ml of the carbon disulphide layer. What is the concentration of iodine in the carbon disulphide layer ?

10.21 (SI Units) When 1 dm^3 of an aqueous solution containing 5 g of a solute is shaken with 50 cm^3 of ether, it is found that 0.84 g of the solute passes into the ether layer. How much of the solute will be left unextracted when the aqueous solution after the first extraction is shaken with a second instalment of 50 cm^3 of ether (assume the solute to have the same molecular state in both water and ether) ?

10.22 (SI Units) The distribution coefficient for ethylacetate between water and benzene is 0.083 at 25°C. If 1 dm^3 of an aqueous solution containing 10 g of ethylacetate is extracted with a total of 300 cm^3 of benzene, how much will be extracted (a) in a single extraction ? (b) in three successive extractions of 100 cm^3 each ?

10.23 An organic compound is extracted from aqueous solution with successive quantities of 25 ml of chloroform. The distribution coefficient of the compound between chloroform and water is 20 : 1. Calculate the number of extractions needed for at least 95% recovery of the compound when the original solution contains 1 g in 500 ml.

10.24 A 500 ml solution containing 100 mg of iodine is shaken with 25 ml of CCl_4 and then allowed to separate. Calculate the quantity of iodine left in the water layer, given that iodine is 90 times more soluble in CCl_4 than in water. If a second extraction is made from the water layer, using another 25 ml of CCl_4, calculate the quantity of iodine remaining.

10.25 K is the partition coefficient between water and an extracting liquid when a g of solution is present in V ml of water and is shaken with v ml of extracting liquid. Show that the weight of solution extracted in the nth instalment is equal to

$$a\left[1-\left(\frac{KV}{KV+v}\right)^n\right]$$

QUIZ QUESTIONS

Type A: Multiple Choice

10.26 In a binary solution x_1 and x_2 are the mole fractions of the two components having p_1^0 and p_2^0 vapour pressures, respectively. The total pressure above the solution (assuming it to be ideal) is

(a) $\left(p_1^\circ - p_2^\circ\right) x_1 + p_2^\circ$

(b) $p_1^\circ x_1 - p_2^\circ x_2$

(c) $\left(p_2^\circ + p_1^\circ\right) x_2 - x_1 p_2^\circ$

(d) $\left(p_2^\circ - p_1^\circ\right) x_2 - \left(p_1^\circ - p_2^\circ\right) x_1$

10.27 Solutions with components which obey Raoult's law over the entire composition range are said to be

(a) real solutions
(b) dilute solutions
(c) binary solutions
(d) ideal solutions

10.28 In a binary ideal solution having mole fractions x_1 and x_2 the free energy of mixing per mole of solution is given by

(a) $RT[\ln x_1 + \ln x_2]$
(b) $RT[x_1 \ln x_1 + x_2 \ln x_2]$
(c) $R[x_1 \ln x_1 + x_2 \ln x_2]$
(d) $n_1 RT \ln x_1 + n_2 RT \ln x_2$

10.29 Which of the following thermodynamic functions of mixing is not correct (for an ideal solution) ?

(a) $\Delta H_m = 0$
(b) $\Delta V_m = 0$
(c) $\Delta S_m = - R[x_1 \ln x_1 + x_2 \ln x_2]$
(d) $\Delta G_m = 0$

10.30 Which of the following systems has lower as well as upper consolute temperatures ?

(a) nicotine–water
(b) aniline–water
(c) triethylamine–water
(d) phenol–water

10.31 The temperature at which two conjugate solutions change into one homogeneous solution is called the

(a) azeotrope
(b) conjugate temperature
(c) consolute temperature
(d) transition temperature

10.32 For a solution of A and B with mole fractions of components x_A and x_B, and activity coefficients γ_A and γ_B, respectively, the Gibbs free energy of mixing is,

(a) $RT[x_A \gamma_A \ln x_A \gamma_A + x_B \gamma_B \ln x_B \gamma_B]$
(b) $-RT[x_A \ln x_A \gamma_A + x_B \ln x_B \gamma_B]$
(c) $-RT[x_B \ln x_A \gamma_A + x_A \ln x_B \gamma_B]$
(d) $-R[x_A \ln x_A \gamma_A + x_B \ln x_B \gamma_B]$

10.33 The law which relates the solubility of a gas to its pressure is called

(a) Raoult's law
(b) The distribution law
(c) Henry's law
(d) Ostwald's law

10.34 If one component obeys Raoult's law over the entire range of compositions-then, for an ideal solution,

(a) the second component must obey Henry's law over the entire composition range
(b) the second component must obey Raoult's law over the entire composition range
(c) both components should obey Henry's and Raoult's law
(d) none of the above is correct

10.35 Which of the following is not the correct criteria for an ideal solution ?
(a) Enthalpy of mixing = 0
(b) Volume of mixing = 0
(c) Free energy of mixing = 0
(d) Obeys Raoult's law

10.36 When a solute S exists as such in phase I and associates in phase II forming S_n species, then the distribution law can be expressed as

(a) $K = \dfrac{C_{I}}{C_{II}^{n}}$

(b) $K = \left(\dfrac{C_{I}}{C_{II}}\right)^{1/n}$

(c) $K = \dfrac{C_{I}}{C_{II}^{1/n}}$

(d) $K = \dfrac{C_{I}}{nC_{II}}$

10.37 When a solute AB exists as such in phase I, dissociates in phase 2 as $A+B$, and α is the degree of dissociation, then the distribution law may be expressed as

(a) $K = \dfrac{C_1}{C_2\,(1-\alpha)}$

(b) $K = \left(\dfrac{C_1}{C_2}\right)^{\alpha}$

(c) $K = \dfrac{C_1}{\alpha C_2}$

(d) $K = \dfrac{C_1}{(C_2)^{1/\alpha}}$

10.38 If w g of solute is present in V_1 ml of water and is shaken with V_2 ml of organic liquid, then the weight of solute left after the third extraction is equal to

(a) $w\left(\dfrac{KV_2}{KV_2+V_1}\right)^3$

(b) $\dfrac{w}{3}\left(\dfrac{KV_2}{KV_2+V_1}\right)$

(c) $w\left(\dfrac{KV_2}{KV_2+KV_1}\right)^3$

(d) $w\left(\dfrac{KV_2}{(KV_2+V_1)^3}\right)$

10.39 In the case of solutions having maxima above the vapour pressure of the pure components, the azeotrope will boil at temperatures
(a) higher than the component having the lower vapour pressure
(b) higher than the component having the higher vapour pressure
(c) lower than both the components
(d) lower than the component of higher vapour pressure and higher than the other

10.40 According to Henry's law, the mole fraction (x) of a gas dissolved in a solvent is related to the pressure of the gas as
(a) $x = k/p$
(b) $x = p/k$
(c) $x = k\sqrt{p}$
(d) $p = k/x$

10.41 Under constant pressure, the solubility of a gas
- (a) increases with increase in temperature
- (b) decreases with increase in temperature
- (c) is generally independent of temperature
- (d) increases with increase in temperature at first and then becomes constant

10.42 For ideal solutions, the volume of mixing is
- (a) $-R\,[x_1 \ln x_1 + x_2 \ln x_2]$
- (b) $-RT\,[x_1 \ln x_1 + x_2 \ln x_2]$
- (c) $R\,[x_1 \ln x_1 + x_2 \ln x_2]$
- (d) zero

10.43 If a binary solution behaves ideally and x_1 and x_2 are the mole fractions of the two components, then the entropy of mixing per mole is
- (a) zero
- (b) $R\,[x_1 \ln x_1 + x_2 \ln x_2]$
- (c) $-R\,[x_1 \ln x_2 + x_2 \ln x_1]$
- (d) $-R\,[x_1 \ln x_1 + x_2 \ln x_2]$

10.44 If a g of solute present in V ml of water is shaken with v ml of chloroform, the weight of solute extracted after the second extraction is equal to (distribution coefficient between chloroform and water is 20 : 1)
- (a) $a\left(\dfrac{V}{V+20v}\right)^2$
- (b) $a\left[1-\left(\dfrac{V}{V+20v}\right)^2\right]$
- (c) $a\left(\dfrac{20V}{20V+v}\right)^2$
- (d) $a\left[1-\left(\dfrac{20V}{20V+v}\right)^2\right]$

10.45 Mixtures corresponding to either a minimum or maximum in boiling point curves are called
- (a) eutectic mixtures
- (b) azeotropic mixtures
- (c) consolute mixtures
- (d) ideal mixtures.

Type B: Multiple Choice (Numerical Problems)

10.46 The vapour pressure of a pure liquid at 25°C is 100 torr. Its mole fraction in the solution is 0.20. If its activity coefficient is 1.5 then its vapour pressure is:
- (a) 30 torr
- (b) 7.5 torr
- (c) 13.3 torr
- (d) 60 torr

10.47 The vapour pressures of pure components A and B are 100 torr and 80 torr respectively. What will be the total pressure of the solution obtained by mixing 2 moles of A and 3 moles of B ?
- (a) 48 torr
- (b) 108 torr
- (c) 88 torr
- (d) 8 torr

10.48 The vapour pressures of pure components '1' and '2' are 200 torr and 100 torr, respectively. Assuming a solution of these components obeys Raoult's law, the mole fraction of component '1' in vapour phase in equilibrium with a solution containing equimoles of 1 and 2 is:

(a) 0.33
(b) 0.66
(c) 0.80
(d) 0.50

10.49 The free energy change of mixing for an ideal binary solution at 27°C is -0.990 kcal mol^{-1}. The entropy change of mixing is

(a) -1.980 kcal mol^{-1}
(b) 3.3 cal mol^{-1} K^{-1}
(c) 9.90 cal mol^{-1} K^{-1}
(d) 0.010 kcal K^{-1} mol^{-1}

10.50 One litre of water under 1.8 atm pressure of gas X dissolves 0.028 g of the gas at 20°C. The Henry's law constant for gas in water is

(a) 1×10^{5} atm
(b) 0.5×10^{-5} atm
(c) 1×10^{-5} atm
(d) 2.5×10^{5} atm

10.51 The Henry's law constant for argon in water is 2.5×10^{4} atm at 25°C. The mole fraction of argon, at an argon pressure of 10 atm, at this temperature, is

(a) 4×10^{-2}
(b) 2.5×10^{3}
(c) 4×10^{-4}
(d) 2.5×10^{5}

10.52 A solute x exists as the monomer in liquid A and dimer in liquid B. The concentrations of the solute in A and B are 0.080 and 0.160 mol l^{-1}, respectively. The distribution coefficient between liquids A and B is

(a) 0.50
(b) 0.20
(c) 0.32
(d) 0.128

10.53 The molality of a solution containing 18 g of glucose (molar mass 180) in 500 g of water is

(a) 1 m
(b) 0.5 m
(c) 0.2 m
(d) 1.2 m

10.54 An aqueous solution contains one gram of a substance in one litre. The solution is shaken twice with ether, using 100 ml ether each time. Calculate the amount of substance extracted if the distribution coefficient of the substance between ether and water is 10 (assume the same molecular state for the solute in both solvents)

(a) 0.25 g
(b) 0.5 g
(c) 0.75 g
(d) 0.85 g

10.55 The partition coefficient of a substance between $CHCl_3$ and H_2O is 5. The amount of substance left unextracted in a solution of 800 mg in 500 ml, after shaking with 100 ml of $CHCl_3$ is

(a) 200 mg
(b) 400 mg
(c) 600 mg
(d) 700 mg

Type C: True or False

10.56 The activity of a component obeying Raoult's law is equal to its mole fraction.

10.57 For an ideal solution, the Gibbs free energy of mixing and the volume of mixing are zero.

10.58 The solubility of a gas in a liquid increases with increase in pressure over the solution, at a given temperature.

10.59 In a binary system, if one component obeys Raoult's law over a certain range of compositions, the other component must obey Henry's law in that composition range.

10.60 According to Henry's law, at constant temperature and pressure, the solubility of all gases in a given liquid is the same.

10.61 Solutions having positive deviations from Raoult's law cannot be distilled into pure components.

10.62 In boiling point composition curves, vapour-composition curves lie above liquid-composition curves.

10.63 The distribution law takes into account the concentrations of similar molecular species in two immiscible liquids.

10.64 All solutions have azeotropes.

10.65 All solutions must obey either Henry's law or Raoult's law over the entire composition range.

Type D: Fill in the Blanks

10.66 The ratio of the concentrations of a solute, in a pair of immiscible liquids, is called ————.

10.67 Ideal solutions obey ———— law.

10.68 Partially miscible liquids are completely miscible at ————.

10.69 If two pure liquids are mixed to give an ideal solution, then ———— and ———— are zero.

10.70 Mixtures which, like pure chemical compounds, boil at a constant temperature and distil over without change in composition are called ————.

ANSWERS

Numerical Problems

10.1 0.238 M, 0.245 m *10.2* 3.67 M, 4.37 m *10.3* 0.2 m, 0.0036 *10.4* 2.06 M *10.5* 0.06 M, 0.076 m, 0.37, 0.83 wt% *10.6* 8.9 g *10.7* (i) 7.22 kPa (ii) 0.20 *10.8* 0.238, 0.762 *10.9* 0.317, 0.540 *10.10* -306.8 cal mol^{-1}, -331.8 cal mol^{-1}, $\Delta G_m^E = 25.0$ cal mol^{-1} *10.11* 177.4 J mol^{-1} *10.12* (a) Chlorobenzene 53.3%, water = 46.7% (b) 106.4; 207.5 torr *10.13* 0.53, 0.47 *10 14* 6.98 g *10.15* 0.832 g *10.16* 1141.1 torr, 76 torr *10.17* $a_A = 0.33$, $a_B = 0.375$, $\gamma_A = 0.66$, $\gamma_B = 0.75$ *10.18* 0.00533 moles *10.19* $C_1/\sqrt{C_2}$ is constant, 9.12, 9.15, 9.13 *10.20* 12 g *10.21* 0.7 g *10.22* (a) 0.783 g (b) 0.907 g *10.23* 5 *10.24* 18.2 mg, 3.31 mg

Quiz Questions

10.26 (a) *10.27* (d) *10.28* (b) *10.29* (d) *10.30* (a) *10.31* (a) *10.32* (b) *10.33* (c) *10.34* (b) *10.35* (c) *10.36* (b) *10.37* (a) *10.38* (a) *10.39* (c) *10.40* (b) *10.41* (a) *10.42* (d) *10 43* (d) *10.44* (b) *10.45* (b) *10.46* (a) *10.47* (c) *10 48* (b) *10.49* (b) *10.50* (a) *10.51* (c) *10.52* (b) *10 53* (c) *10.54* (c) *10.55* (b) *10.56* True *10.57* False: Volume of mixing is zero but Gibbs free energy change of mixing is not zero *10.58* True *10.59* True *10.60* False *10.61* True *10 62* True *10.63* True *10.64* False *10.65* False *10.66* partition coefficient *10.67* Raoult's *10.68* Critical solution temperature *10.69* Enthalpy of mixing, volume of mixing *10.70* azeotropic mixtures.

11

Colligative Properties and Dilute Solutions

Dilute solutions containing non-volatile solutes exhibit four important properties; i.e. relative lowering of vapour pressure of solvent, elevation of boiling point, depression of freezing point and osmotic pressure. These properties are called colligative properties. For dilute solutions, colligative properties depend on the nature of the solvent and number of particles* of the solute, but not on its nature. These properties are very useful in determining the molar masses of nonvolatile solutes and their behaviour (associated or dissociated) in solutions. The methods can also be used to determine the activity coefficients of the solutes.

11.1 RELATIVE LOWERING OF VAPOUR PRESSURE

The addition of a nonvolatile solute to a solvent lowers its vapour pressure. If x_1 is the mole fraction of the solvent, x_2 the mole fraction of the solute, p° the vapour pressure of the pure solvent, and p the vapour pressure of the solution, then, according to Raoult's law, the vapour pressure of the solution, p is given by the relation,

$$p = p^\circ x_1 \tag{11.1}$$

Since x_1 is always less than one, the vapour pressure of the solution is always less than p° (vapour pressure of the pure solvent). The relative lowering in vapour pressure ($\Delta p/p^\circ$) is given by the equation:

$$\frac{\Delta p}{p^\circ} = \frac{p^\circ - p}{p^\circ} = \frac{p^\circ - x_1\, p^\circ}{p^\circ} = x_2 \tag{11.2}$$

Relative lowering of vapour pressure is, therefore, independent of the nature of the solute and solvent and depends only on the mole fraction of the solute. Thus, it is a colligative property. If w_1 and w_2 are the weights of solvent and the solute, and M_1 and M_2 are their corresponding molar masses, then

Mole fraction of solute, $$x_2 = \frac{w_2/M_2}{w_1/M_1 + w_2/M_2} \tag{11.3}$$

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*Particles mean all species (molecules, ions, etc.) which exist independently in the solution.

For dilute solutions,

$$\simeq \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 M_1}{w_1 M_2} \qquad (w_2 \ll w_1)$$

Therefore, $$\frac{\Delta p}{p^\circ} = \frac{w_2 M_1}{w_1 M_2}$$

or $$M_2 = \frac{w_2 M_1}{w_1 \times \Delta p/p^0} \tag{11.4}$$

With the help of Eq. (11.4), the molar mass of the solute can be determined if the other quantities on the right-hand side are known. More precisely, molar mass M_2 can be calculated from the relation [obtained from Eq. (11.3)],

$$M_2 = \frac{w_2}{w_1} M_1 \left(\frac{p^\circ}{\Delta p} - 1 \right) \tag{11.5}$$

11.2 DETERMINATION OF LOWERING OF VAPOUR PRESSURE

Two methods are generally used

Differential (or Static Method)

In this method, the difference in vapour pressure between the pure solvent and the solution is measured by connecting these to the two sides of a differential manometer. The accuracy of the measurements can be increased by using manometric liquids (e.g., silicon oils) of lower density than mercury.

Dynamic Method

This is used mostly for aqueous solutions. In this method, a stream of dry air is bubbled successively through the solution and the pure solvent, which removes water. The loss of water from the solution and solvent is noted. These are proportional to p and $(p^\circ - p)$ respectively.

EXAMPLE 11.1 The vapour pressure of water at 20°C is 17.51 torr. The lowering of vapour pressure of a sugar solution is 0.0614 torr. Calculate

(a) the relative lowering of vapour pressure
(b) the vapour pressure of the solution
(c) the mole fraction of water

Solution (a) Relative lowering of vapour pressure $= \frac{\Delta p}{p^0}$.

Lowering of vapour pressure, $\Delta p = 0.0614$ torr, $p^\circ = 17.51$ torr

$$\frac{\Delta p}{p^\circ} = \frac{0.0614}{17.51} = 0.0035$$

(b) Vapour pressure of solution $= p^\circ - \Delta p$

$$= 17.51 - 0.0614 = 17.45 \text{ torr}$$

(c) Mole fraction of solute, $x_2 = \dfrac{\Delta p}{p^\circ} = 0.0035$

Mole fraction of water $= 1 - x_2 = 1 - 0.0035$

$$= 0.9965$$

Example 11.2 (SI Units) The vapour pressure of pure water at 298 K is 3.16×10^3 N m^{-2} and the vapour pressure of a solution containing 5.30 g per 100 g water, at 298 K, is 3.11×10^3 N m^{-2}. Calculate the molar mass of the solute.

Solution Molar mass of the solute,

$$M_2 = \frac{w_2\, M_1\, p^\circ}{w_1\, \Delta p}$$

Vapour pressure of pure water, $p^\circ = 3.16 \times 10^3 \text{ N m}^{-2}$

Vapour pressure of solution, $p = 3.11 \times 10^3 \text{ N m}^{-2}$

Lowering of vapour pressure, $\Delta p = (3.16 - 3.11) \times 10^3$

$$= 0.05 \times 10^3 = 50 \text{ N m}^{-2}$$

Weight of solute, $w_2 = 5.30$ g

Wt. of solvent, $w_1 = 100$ g

Molar mass of water, $M_1 = 18 \times 10^{-3}$ kg mol^{-1}

$$\therefore \quad M_2 = \frac{(5.30 \text{ g}) \times (18 \times 10^{-3} \text{ kg mol}^{-1}) \times (3.16 \times 10^3 \text{ N m}^{-2})}{(100 \text{ g}) \times (50 \text{ N m}^{-2})}$$

$$= 60.3 \times 10^{-3} \text{ kg mol}^{-1}$$

Molar mass $= 60.3$

Example 11.3 *Dry air, when bubbled through a solution and later through pure water at 25°C, causes a loss of 1.0180 g and 0.0435 g, respectively. If the solution contains 133.3 g of the solute in 1000 g of water, calculate the molar mass of the solute.*

Solution Molar mass of solute,

$$M_2 = \frac{w_2\, M_1\, p^\circ}{w_1\, \Delta p}$$

Loss in solution bulbs $= 1.0180$ g

Loss in water bulbs $= 0.0435$ g

Total loss $= 1.0180 + 0.0435 = 1.0615$ g

Relative lowering of vapour pressure,

$$\frac{\Delta p}{p^\circ} = \frac{\text{Loss in water bulbs}}{\text{Total loss}} = \frac{0.0435}{1.0615}$$

Wt. of solute, $w_2 = 133.3$ g

Wt. of solvent, $w_1 = 1000$ g

Molar mass of water, $M_1 = 18$

$$M_2 = \frac{133.3 \times 18 \times 1.0615}{1000 \times 0.0435} = 58.6$$

11.3 ELEVATION OF BOILING POINT

The vapour pressure of a solution is less than that of the pure solvent. Therefore, the solution has to be heated to a higher temperature for its vapour pressure to become equal to atmospheric pressure (boiling point). Thus, the boiling point of the solution will be higher than that of the solvent. The difference between the boiling points of the solution (T_b) and the pure solvent (T_b°) at any given pressure is termed as the *elevation in boiling point* (ΔT_b).

$$\Delta T_b = \frac{RT_b^{\circ 2}}{\Delta H_{\text{evap}}} x_2 \tag{11.6}$$

where ΔH_{evap} is the enthalpy of evaporation of the pure solvent. As, for a given solvent, T_b° and ΔH_{evap} are constant, the elevation in boiling point is directly proportional to the mole fraction of the solute only. Thus, it is a colligative property. In terms of molality (moles of solute per thousand grams of the solvent) m,

$$T_b \simeq K_b\, m \tag{11.7}$$

where K_b is the molal boiling point elevation constant or *ebulloscopic constant* and is expressed as

$$K_b = \frac{RT_b^{\circ 2} \times M_1}{\Delta H_{\text{evap}} \times 1000} = \frac{RT_b^{\circ 2}}{\Delta h_{\text{evap}} \times 1000} \tag{11.8}$$

where $\Delta h_{\text{evap}} = \dfrac{\Delta H_{\text{evap}}}{M_1}$ (enthalpy of evaporation per gram)

Knowing K_b and ΔT_b, the molar mass of solute can be calculated from the relation,

$$M_2 = \frac{K_b \times 1000\, w_2}{w_1 \times \Delta T_b} \tag{11.9}$$

11.4 MEASUREMENT OF THE ELEVATION OF BOILING POINT

There are two methods.

Landsberger's Method

In this method, the boiling point of the solvent is determined by raising its temperature by the condensation of the solvent from another flask. The latent heat of condensation raises the temperature of the solvent to boiling point. A weighed amount of solute is then added and the boiling point of the solution determined again.

Cottrell's Method

In this method, the thermometer is kept at such a position that when the liquid in the tube starts boiling, the bulb of the thermometer is bathed in the boiling solution. After determining the boiling point of the solvent, a known weight of solute is added and its boiling point determined. This method is more accurate.

EXAMPLE 11.4 (SI Units) Calculate the ebulloscopic constant for benzene from the following data:

Boiling point, $T_b = 353$ K, $\Delta H_{\text{evap},\,m} = 30.8$ kJ mol^{-1}

Solution Ebulloscopic constant,

$$K_b = \frac{RT_b^{\circ 2}M}{1000\,\Delta H_{\text{evap},\,m}}$$

$$R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1},\ T_b = 353\ \text{K},$$

$$\Delta H_{\text{evap},\,m} = 30.8\ \text{kJ mol}^{-1}$$

$$M = 78\ \text{g mol}^{-1}$$

$$K_b = \frac{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\times(353\ \text{K})^2\times(78\ \text{g mol}^{-1})}{1000\ \text{g/kg}\times(30.8\times10^3\ \text{J mol}^{-1})}$$

$$= 2.62\ \text{K mol}^{-1}\ \text{kg} \quad \text{or} \quad 2.62\ \text{K/(mol kg}^{-1})$$

or $$= 2.62\ \text{K}m^{-1} \qquad [m = \text{mol kg}^{-1}]$$

EXAMPLE 11.5 The latent heat of vaporization of water is 539 cal g^{-1} and the boiling point 100°C. Calculate the boiling point of an aqueous solution containing 10 g of urea (molar mass = 60) in 250 g of water.

Solution The change in boiling point,

$$\Delta T_b = K_b\,m$$

$$m = \frac{\text{moles of urea}}{\text{kg water}} = \frac{10/60}{250\times10^{-3}}$$

$$= 0.667\ \text{mol kg}^{-1}$$

$$K_b = \frac{RT_b^{\circ 2}}{1000\ \Delta h_{\text{evap},\,m}}$$

$$R = 1.98\ \text{cal mol}^{-1}\ \text{K}^{-1},\ T_b^\circ = 100+273 = 373\ \text{K},$$

$$\Delta h_{\text{evap},\,m} = 539\ \text{cal g}^{-1}$$

$$K_b = \frac{(1.98\ \text{cal mol}^{-1}\ \text{K}^{-1})\times(373\ \text{K})^2}{(1000\ \text{g/kg})\times(539\ \text{cal g}^{-1})}$$

$$\doteq 0.511\ \text{K mol}^{-1}\ \text{kg}$$

or $$= 0.511\ \text{K/(mol kg}^{-1})$$

Now, $$\Delta T_b = K_b\,m$$

$$= (0.511\ \text{K kg mol}^{-1})\times(0.667\ \text{mol kg}^{-1})$$

$$= 0.34\ \text{K}$$

Change in boiling point = 0.34°

Thus, the aqueous solution will boil at

$$T = T_b^\circ + \Delta T_b = 100+0.34$$

or
$$T = 100.34^\circ\text{C}$$

EXAMPLE 11.6 The boiling point of a solution containing 2.56 g of a substance X per 100 g of water is higher by 0.052°C than the boiling point of pure water. Calculate the molar mass of the substance if the ebulloscopic constant of water is 5.12 K/(mol/100 g).

Solution Molar mass of the compound,

$$M_2 = K_b \frac{1000\, w_2}{\Delta T_b\, w_1}$$

$$\Delta T_b = 0.052, \quad w_2 = 2.56\text{ g}, \quad w_1 = 100\text{ g}$$

$$K_b = 5.12\text{ K/(mol/100 g)} = 0.512\text{ K/(mol kg}^{-1})$$

$$M_2 = \frac{0.512\times 1000\times 2.56}{0.052\times 100} = 252.1$$

Note: One should be careful while using the value of K_b or K_f. It may be expressed as K/(mol per 1000 g), i.e. K/(mol per kg) or K/(mol per 100 g). The value in the latter case is ten times the value in the former case, e.g. K_b for water is 0.512 K/(mol kg^{-1}) or 5.12 K per mol per 100 g.

11.5 DEPRESSION IN FREEZING POINT

The freezing point is the temperature at which the vapour pressures of the solid and liquid states are the same. The vapour pressure of the solution is less than that of the solvent. Therefore, it can be in equilibrium with the solid phase at a lower pressure and hence, at a lower temperature. The difference in freezing points of the solution (T_f) and the pure solvent (T_f°) at a given pressure is referred to be the *depression in freezing point* (ΔT_f).

$$\Delta T_f = \frac{RT_f^{\circ 2}}{\Delta H_{\text{fus}}}\, x_2 \tag{11.10}$$

where ΔH_{fus} is the enthalpy of fusion of the solvent. Since, for a given solvent, T_f° and ΔH_{fus} are constant, the depression in freezing point depends only on the mole fraction of the solute. Hence, it is a colligative property. It may also be expressed as

$$\Delta T_f = K_b\, m \tag{11.11}$$

where K_f is the *molal freezing point depression constant* or the *cryoscopic constant* and is expressed as

$$K_f = \frac{RT_f^{\circ 2} M_1}{\Delta H_{\text{fus}}\times 1000} = \frac{RT_f^{\circ 2}}{\Delta h_{\text{fus}}\, 1000} \tag{11.12}$$

where $\Delta h_{fus} = \frac{\Delta H_{fus}}{M_1}$ is the enthalpy of fusion per gram.

Knowing K_f and the depression in freezing point, the molar mass of the solute (M_2) can be calculated from the relation

$$M_2 = K_f \frac{1000\, w_2}{\Delta T_f\, w_1} \tag{11.13}$$

11 6 DETERMINATION OF DEPRESSION IN FREEZING POINT

Depression in freezing point is measured by the Beckmann method. A known weight of the solvent is taken in a tube known as a freezing point tube. It is cooled, with constant stirring, to about 0.5° below its freezing point (super cooling). Then, with rigorous stirring, the temperature of the solvent rises to the freezing point (appearance of crystals of the solvent). A known weight of the solute is added and the freezing point of the solution determined. The difference between these gives the depression in freezing point.

Example 11.7 The enthalpy of fusion of benzene is 30.05 cal g^{-1} and it freezes at 5.48°C. What is its molal depression constant ?

Solution Molal depression constant,

$$K_f = \frac{RT_f^{\circ 2}}{\Delta h_{fus}\, 1000}$$

$$R = 1.98 \text{ cal K}^{-1}\text{ mol}^{-1}, \quad T_f^{\circ} = 5.48 + 273 = 278.48 \text{ K}$$

$$\Delta h_{fus} = 30.05 \text{ cal g}^{-1}$$

$$K_f = \frac{(1.98 \text{ cal K}^{-1}\text{ mol}^{-1}) \times (278.48 \text{ K})^2}{(30.05 \text{ cal g}^{-1}) \times (1000 \text{ g/kg})}$$

$$= 5.11 \text{ K kg mol}^{-1} \quad \text{or} \quad = 5.11 \text{ K/(mol kg}^{-1})$$

Example 11 8 (SI Units) The enthalpy of fusion of water at 273 K is 333.86 J g^{-1}. A solution containing 2.5 g of a solute in 100 g of water has a freezing point 0.42 K lower than that of pure water. Calculate the molar mass of the solute.

Solution Molar mass of the solute,

$$M_2 = K_f \frac{1000\, w_2}{w_1 \times \Delta T_f}$$

$$w_2 = 2.50 \text{ g}, \quad w_1 = 100 \text{ g}, \quad \Delta T_f = 0.42 \text{ K}$$

K_f can be calculated as

$$K_f = \frac{RT_f^{\circ 2}}{\Delta h_{fus} \times 1000}$$

$$T_f^{\circ} = 273 \text{ K}, \quad R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1},$$

$$\Delta h_{fus} = 333.86 \text{ J g}^{-1}$$

or $$K_f = \frac{(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (273 \text{ K})^2}{(1000 \text{ J/kg}) \times 333.86 \text{ J g}^{-1}}$$

$$= 1.86 \text{ K/(mol kg}^{-1})$$

$\therefore$ $$M_2 = \frac{(1.86 \text{ K kg mol}^{-1}) \times 1000 \times (2.50 \text{ g})}{(100 \text{ g}) \times (0.42 \text{ K})}$$

$$= 110.7 \text{ g mol}^{-1}$$

or Molar mass = 110.7

EXAMPLE 11.9 The molal depression constant for benzene is 5.12 K kg mol^{-1}. A solution containing 1 g of solute per 100 g of benzene freezes at 5.1°C. What is the molar mass of the solute (freezing point of pure benzene is 5.5°C) ?

Solution Molar mass of solute,

$$M_2 = K_f \frac{1000\, w_2}{w_1 \times \Delta T_f}$$

$$w_1 = 100 \text{ g}, \quad w_2 = 1 \text{ g}, \quad T_f = 5.5 - 5.1 = 0.4°,$$

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

$$M_2 = \frac{(5.12 \text{ K kg mol}^{-1}) \times 1000 \times (1 \text{ g})}{(100 \text{ g}) \times (0.4 \text{ K})}$$

$$= 128 \text{ g mol}^{-1}$$

11.7 OSMOSIS AND OSMOTIC PRESSURE

When a solution is separated from the pure solvent by a semipermeable membrane (which permits the flow of solvent but not of solute), it is observed that the solvent passes through the membrane into the solution. The phenomenon of flow of solvent across a semipermeable membrane, from the pure solvent to the solution side, is called *osmosis*.

The pressure which must be applied to a solution to prevent the flow of solvent into it through the semipermeable membrane is called *osmotic pressure*. Solutions having the same osmotic pressure are called *isotonic* or *isoosmotic*. Obviously, two isoosmotic solutions separated by a semipermeable membrane will show no net flow of solvent.

11 8 VAN'T HOFF LAW FOR OSMOTIC PRESSURE

Van't Hoff (1886) showed that the results of osmotic pressure (π) for any solution could be expressed as

$$\pi = CRT$$

or $$\pi = \left(\frac{n}{V}\right) RT$$

or $$\pi V = nRT \tag{11.14}$$

where C is the concentration of solute (mol l^{-1}), R the gas constant and T the temperature. This shows that osmotic pressure at any given temperature depends upon the molar concentration of the solute only, and hence is a colligative property.

Molar mass can be calculated from osmotic pressure by the relation,

$$M_2 = \frac{RT\,w_2}{\pi V} \tag{11.15}$$

Reverse Osmosis

If, in the case of a solution separated from the pure solvent by a semipermeable membrane, the pressure applied on the solution is more than the osmotic pressure, the solvent will start flowing from the solution towards the pure solvent. This phenomenon is called reverse osmosis. It has acquired importance in the process of converting sea water into fresh water, or concentrating dilute solution without spending too much energy.

11.9 DETERMINATION OF OSMOTIC PRESSURE

Two important methods are used.

Pfeffer's Method

In this method, a porous pot (a semipermeable ferrocyanide membrane is deposited in the pores) is filled with the aqueous solution, sealed at the top, and connected to a manometer. Water seeps inside and the pressure on the manometer increases till a constant value is reached. The final value is the osmotic pressure.

Berkley-Hartley Method

In this method, the solvent is put inside a porous pot with side tubes. This is placed in a bronze vessel containing a solution to which pressure can be applied and measured. Pressure is applied on the solution so that there is no flow of solvent through the semipermeable membrane on either side. This gives the osmotic pressure.

EXAMPLE 11.10 What will be the osmotic pressure of a solution containing 3.42 g of sugar in one dm³ of solution at 27°C (molar mass of sugar = 342)?

Solution Osmotic pressure,

$$\pi V = nRT$$

Moles of sugar dissolved $= \dfrac{3.42 \text{ g}}{342 \text{ g mol}^{-1}} = 0.01$

Volume $V = 1 \text{ dm}^3$

$R = 0.082 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$ and $T = 273+27 = 300$ K

$$= \frac{(0.01 \text{ mol}) \times (0.082 \text{ dm}^3 \text{ atm mol}^{-1} \text{ K}^{-1}) \times (300 \text{ K})}{1 \text{ dm}^3}$$

$$= 0.246 \text{ atm}$$

Example 11.11 (SI Units) The osmotic pressure of a solution containing 5 g sucrose in 250 cm³ is 1.45×10^5 N m^{-2} at 298 K. What is the molar mass of sucrose ?

Solution $\pi V = nRT$

$$= \frac{w_2 RT}{M_2 V}$$

or $$M_2 = \frac{w_2 RT}{\pi V}$$

$$w_2 = 5 \text{ g}, \; V = 250 \text{ cm}^3 = 2.5 \times 10^{-4} \text{ m}^3,$$
$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$
$$T = 298 \text{ K}, \quad \pi = 1.45 \times 10^5 \text{ N m}^{-2}$$
$$M_2 = \frac{(5.0 \text{ g}) \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})}{(1.45 \times 10^5 \text{ N m}^{-2}) \times (2.5 \times 10^{-4} \text{ m}^{-3})} \qquad [\text{J} = \text{N m}]$$
$$= 341.7 \text{ g mol}^{-1}$$

or, Molar mass = 341.7

Example 11.12 The average osmotic pressure of human blood at 37°C is 7.6 atm. What will be the total concentration of the various solutes in blood ? What will be the freezing point if the molarity is taken to be equal to molality ($K_f = 1.86$ K/mol kg^{-1})?

Solution Osmotic pressure,

$$\pi = CRT$$

or $$C = \frac{\pi}{RT}$$

$$R = 0.082 \, l \text{ atm K}^{-1} \text{ mol}^{-1},$$
$$T = 273 + 37 = 310 \text{ K}, \quad \pi = 7.6 \text{ atm}$$

$$\therefore \quad C = \frac{7.6 \text{ atm}}{(0.082 \, l \text{ atm K}^{-1} \text{ mol}^{-1}) \times (310 \text{ K})} = 0.299 \text{ mol } l^{-1}$$

Now, molality, $m = 0.299$

$$\Delta T_f = K_f \, m = 1.86 \times 0.299 = 0.556$$

Since freezing point of water is 0 °C, blood will freeze at -0.556°C.

11.10 COLLIGATIVE PROPERTIES OF SOLUTIONS IN SOME SPECIAL CASES

Solutions Containing a Mixture of Solutes

Colligative properties depend only on the total number of the particles (molecules, atoms, ions or aggregates) and therefore will depend on the number of molecules from the different solutes present. When two or more solutes are present, the relations become

(a) Relative lowering of vapour pressure,

$$\frac{\Delta p}{p^\circ} = \frac{\Sigma m_i \times M_i}{1000}$$ (where m_i is the molality of each solute and M_i its molar mass)

(b) Elevation of boiling point

$$\Delta T_b = K_b \, \Sigma m_i$$

(c) Depression in freezing point

$$\Delta T_f = K_f \, \Sigma m_i$$

(d) Osmotic pressure

$$\pi = (\Sigma C_i)\, RT$$ (C_i is the molarity of each solute)

Dissociation of the Solute

Molecules of certain substances (e.g. electrolytes), when dissolved in a solvent, dissociate to give two or more particles. Colligative properties of such solutions are large compared with the values calculated from simple relations. For example, consider the dissociation of AB as

$$AB \rightleftharpoons A^+ + B^-$$

If the degree of dissociation is α and m moles of AB are present in 1000 g of the solvent, then the concentration of species is

$$[AB] = m(1-\alpha)\ ;\ [A^+] = m\alpha\ ;\ [B^-] = m\alpha$$

The sum of the molalities of all species $= m(1-\alpha)+m\alpha+m\alpha = m(1+\alpha)$ Thus, colligative properties will depend on $m(1+\alpha)$ particles rather than m particles. In order to account for abnormal cases, Van't Hoff introduced a factor i known as the *Van't Hoff factor.*

$$i = \frac{\text{Observed property}}{\text{Normal property}} = \frac{\text{Normal molar mass}}{\text{Observed molar mass}}$$

or $$i = \frac{\Delta p}{(\Delta p)_\circ} = \frac{\Delta T_b}{(\Delta T_b)_\circ} = \frac{\Delta T_f}{(\Delta T_f)_\circ} = \frac{\pi}{(\pi)_\circ} = \frac{M_\circ}{M}$$

where the quantities without the zero subscripts refer to experimental observed properties while those with subscripts refer to normal calculated values on the basis of ideal behaviour (i.e. assuming the solute to be nonelectrolyte).

Association of the Solute

There are substances which undergo association in some solvents. For example, benzoic acid dimerizes in nonpolar solvents. The total number of particles will be less than the number of molecules of the substance added and, therefore, colligative properties will be lower. For example, consider

$$2A \rightleftharpoons (A)_2$$

Let m be the molality of the solution and the degree of association p. Then, molality of each species is

$$[A]_2 = mp/2$$
$$[A] = m\,(1-p)$$

$$\text{Sum of molalities} = m\,(1-p)+\frac{mp}{2}$$

$$= m\left(1-\frac{p}{2}\right)$$

Thus, properties will correspond to $m\left[1-\frac{p}{2}\right]$ particles rather than m particles.

Complex Formation

In certain cases, two solutes or their dissociated products may react with each other to give one or more complexes. The molality of each species in the solution will depend on the equilibrium constants of such reactions. Thus, the measurement of any colligative property over a range of concentrations may give us information regarding the possible reactions between different species in the solution and their equilibrium constants.

EXAMPLE 11.13 A solute containing 1.23 g of calcium nitrate in 10 g of water boils at 100.975°C. Calculate the apparent degree of ionization of the salt (K_b for water is 0.52 K mol^{-1} kg).

Solution $\Delta T_b = K_b \dfrac{1000\, w_2}{M_2\, w_1}$

Observed molar mass, $M_2 = K_b \dfrac{1000\, w_2}{\Delta T_b\, w_1}$

$$w_1 = 10\text{ g},\quad w_2 = 1.23\text{ g},\quad \Delta T_b = 100.975-100 = 0.975,$$

$$K_b = 0.52°\text{ K mol}^{-1}\text{ kg}$$

$$\therefore M_2 = \frac{(0.52\text{ K mol}^{-1}\text{ kg})\times 1000\times(1.23\text{ g})}{(0.975\text{K})\times(10.0\text{ g})} = 65.6$$

Normal molar mass = 164

$$\text{Van't Hoff factor } i = \frac{\text{Normal molar mass}}{\text{Observed molar mass}} = \frac{164}{65.6}$$

Now, $Ca(NO_3)_2 \rightleftharpoons Ca^{2+} + 2NO_3^-$

If α is the degree of ionization,

$$\underset{(1-\alpha)}{Ca(NO_3)_2} \rightleftharpoons \underset{\alpha}{Ca^{2+}} + \underset{2\alpha}{2\,NO_3^-}$$

$$i = \frac{1-\alpha+\alpha+2\alpha}{1} = \frac{164}{65.6}$$

or $$1 + 2\alpha = \frac{164}{65.6}$$

$$\alpha = 0.75$$

Degree of ionization of $Ca(NO_3)_2$ = 75.0%

EXAMPLE 11.14 A decimolar solution of potassium ferrocyanide $K_4[Fe(CN)_6]$ is 46% dissociated at 290 K. Calculate the osmotic pressure of the solution.

Solution The osmotic pressure,

$$\pi V = n\,RT$$

$$n = 0.1 \text{ mol},\quad V = \ \text{dm}^3 = 1\times10^{-3}\text{ m}^3,$$

$$R = 8.314 \text{ J K}^{-1}\text{ mol}^{-1},\ T = 290 \text{ K}$$

$$\therefore \quad \pi = \frac{nRT}{V} = \frac{(0.1 \text{ mol})\times(8.314 \text{ J K}^{-1}\text{ mol}^{-1})\times(290\text{ K})}{1\times10^{-3}\text{ m}^3}$$

$$= 2.41\times10^{5}\text{ N m}^{-2} \qquad (\text{J} = \text{N m})$$

Let α be the degree of dissociation

$$K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN_6)]^{4-}$$

After dissociation: $1-\alpha$ $\quad 4\alpha \quad \alpha$

Particles after dissociation $= 1-\alpha+4\alpha+\alpha = 1+4\alpha$

Van't Hoff factor $i = \dfrac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \dfrac{1+4\alpha}{1}$

$$\alpha = 46\% = 0.46$$

Normal osmotic pressure $= 2.41\times10^5\text{ N m}^{-2}$

$$\frac{\text{Observed osmotic pressure}}{2.41\times10^5\text{ N m}^{-2}} = \frac{1+4\times0.46}{1}$$

Observed osmotic pressure $= 2.41\times10^5\times2.84$

$$= 6.84\times10^5\text{ N m}^{-2}$$

EXAMPLE 11.15 Phenol associates in benzene to form the dimer $(C_6H_5OH)_2$. The freezing point of a solution containing 5 g of phenol in 250 g of benzene is lowered by 0.70°. Calculate the degree of association of phenol in benzene (K_f for benzene $= 5.12$ K mol^{-1} kg).

Solution Let us first calculate the observed molar mass,

$$M_2 = K_f\,\frac{1000 w_2}{\Delta T_f\, w_1}$$

$$K_f = 5.12\text{ K mol}^{-1}\text{ kg},\quad w_2 = 5\text{ g},\quad w_1 = 250\text{ g},$$

$$\Delta T_f = 0.70$$

$$M_2 = \frac{5.12\times1000\times5}{0.70\times250} = 146.3$$

Let degree of association of phend $= x$

Phenol associates as

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

Particles after association, $\quad 1-x \qquad x/2$

Total particles after association $= 1 - x + \dfrac{x}{2} = 1 - \dfrac{x}{2}$

Now, $\dfrac{\text{Normal molar mass}}{\text{Observed molar mass}} = \dfrac{\text{Particles after association}}{\text{Normal particles}}$

Normal molar mass $= 94$

or $$\frac{94}{146.3} = \frac{1-(x/2)}{1}$$

or $$x = 0.715$$

Thus, degree of association of phenol $= 71.5\%$

MISCELLANEOUS EXAMPLES

EXAMPLE 11.16 An aqueous solution freezes at −0.20°C. What is the molality of the solution ? Also calculate

(a) Elevation in boiling point

(b) Lowering of vapour pressure at 25°C

Given that $K_f = 1.86$ K mol^{-1} kg, $K_b = 0.512$ K mol^{-1} kg and vapour pressure of water at 25°C = 23.756 torr.

Solution Freezing point of water =0°C

Freezing point of solution = − 0.20°C

Lowering in freezing point, $\Delta T_f = 0.20$°C

Now, $\Delta T_f = K_f m$

or $$m = \frac{\Delta T_f}{K_f} = \frac{0.20}{1.86} = 0.107$$

(a) Elevation in boiling point,

$$\Delta T_b = K_b m = 0.512 \times 0.107 = 0.0548°\text{C}$$

(b) Lowering of vapour pressure,

$$\frac{\Delta p}{p°} = x_2 \simeq \frac{m}{1000/M_1} = \frac{0.107 \times 18}{1000}$$

$$p° = 23.756 \text{ torr.}$$

$$\therefore \quad \Delta p = \frac{0.107 \times 18 \times 23.756}{1000} = 0.0458 \text{ torr}$$

EXAMPLE 11.17 A solution containing 5% of a substance X is isotonic with a solution containing 10 g of urea per litre. Calculate the molar mass of substance X.

Solution The solutions are isotonic,

$$\pi \text{ (substance } X) = \pi \text{ (urea)}$$

A 5% solution of substance X contains 5 g of substance X in 100 ml of solution.

$$n = \frac{5}{M}, \quad V = 100 \text{ ml}$$

$$\pi \text{ (substance } X) = \frac{nRT}{V} = \frac{5}{100\,M} RT$$

For urea solution,

$$n = \frac{10}{60}, \quad V = 1000 \text{ ml}$$

$$\therefore \quad \pi \text{ (urea)} = \frac{10}{60 \times 1000} RT$$

Thus, $$\frac{5}{100\,M} = \frac{10}{60 \times 1000}$$

or $$M = 300$$

Molar mass of compound = 300

EXAMPLE 11.18 The latent heat of vaporization of carbon disulphide is 85.9 cal g^{-1} and its boiling point is 46.2°C. A solution of 0.938 g benzoic acid in 50 g of CS_2 boils at 46.38°C. Calculate the apparent molar mass of benzoic acid. On the basis of this result, what can you comment about the molecular state of benzoic acid in this solvent ?

Solution Molar mass of benzoic acid,

$$M_2 = \frac{K_b \times w_2 \times 1000}{\Delta T_b \times w_1}$$

$$T_b^\circ = 46.2^\circ\text{C}, \quad T_b = 46.38^\circ\text{C},$$

$$\Delta T_b = 46.38 - 46.2 = 0.18$$
$$w_1 = 50 \text{ g}, \quad w_2 = 0.938 \text{ g}$$

K_b can be calculated as

$$K_b = \frac{RT_b^{\circ 2}}{\Delta h_v \times 1000}$$

$$R = 1.98 \text{ cal K}^{-1} \text{ mol}^{-1}, T_b^\circ = 46.2 + 273 = 319.2 \text{ K}$$

$$\Delta h_v = 85.9 \text{ cal g}^{-1}$$

$$K_b = \frac{1.987 \times (319.2)^2}{85.9 \times 1000} = 2\ 35 \text{ K mol kg}^{-1}$$

$$M_2 = \frac{(2.35 \text{ K mol kg}^{-1}) \times (0.9380 \text{ g}) \times 1000}{(0.18 \text{ K}) \times (50.0 \text{ g})}$$
$$= 244.9$$

Since the observed molar mass of benzoic acid is almost twice than the actual molar mass (122), the solute exists as a dimer.

EXAMPLE 11.19 In cold climates, the water in a car gets frozen causing damage to the radiator. Ethylene glycol is used as an antifreezing agent. Estimate the amount of ethylene glycol that should be added to 5 kg of water to prevent it from freezing at − 7°C. (K_f for water $= 1.85$ K mol^{-1} kg).

Solution $\Delta T_f = K_f \left(\dfrac{1000 \times w_2}{M_2\, w_1} \right)$

$$\Delta T_f = 7 \text{ K}, \quad K_f = 1.86 \text{ K mol}^{-1} \text{ kg}, w_2 = ?, w_1 = 5 \times 10^3 \text{ g}$$
$$M_2 = 62$$

$$\therefore \quad w_2 = \frac{\Delta T_f\, M_2\, w_1}{1000\, K_f}$$

$$= \frac{7 \times 62 \times 5 \times 10^3}{1.86 \times 1000} = 1167 \text{ g} = 1.167 \text{ kg}$$

EXAMPLE 11.20 A solution containing 25 g of ethylene glycol in 100 ml of water is cooled to − 10°C. How much ice will separate ? The molal freezing point depression constant K_f for water $= 1.86$ K mol^{-1} kg.

Solution At −10°C, ice crystallises out from an aqueous solution. The weight of ethylene glycol remains the same as initially present. Weight of ethylene glycol initially present = 25 g per 100 g of water.

Now, $\Delta T = K_f \, m$

$$\Delta T = 10, \quad K_f = 1.86 \text{ K mol}^{-1} \text{ kg}$$

$$m = \frac{\Delta T}{K_f} = \frac{10}{1.86} = 5.38 \text{ mol kg}^{-1}$$

At −10°C, 5.38 mol or 5.38 × 62 g of ethylene glycol is present in 1000 g of water.

25 g of ethylene glycol will be present in $= \dfrac{1000}{5.38 \times 62} \times 25$

$$= 74.95 \text{ g of water}$$

Weight of ice separated at $-10°\text{C} = 100 - 74.95 = 25.05$ g

QUESTIONS

Numerical Problems

11.1 (SI Units) The vapour pressure of water at 298 K is 3.15×10^3 N m^{-2}. Calculate the vapour pressure of a solution containing 3 g of urea in 100 g of water.

11.2 The vapour pressure of pure water at 25°C is 23.756 torr and that of a solution containing 5 g of solute in 100 g of water is 23.402 torr. Calculate the molar mass of the solute.

11.3 A current of dry air was passed through a series of bulbs containing a solution of 4.206 g of a substance in 100 g of ethyl alcohol, and then through pure ethyl alcohol. The loss in weight of the former was 1.0165 g, and in the latter was 0.0425 g. Calculate the molar mass of the solute.

11.4 (SI Units) At a certain temperature, the vapour pressure of water is 1.22×10^4 N m^{-2}. On dissolving 18.2 g of a non-electrolyte *A* in 100 g of water, the solution had a vapour pressure of 1.16×10^4 N m^{-2}. What is the molar mass of *A* ?

11.5 Calculate the ebullioscopic constant for benzene and carbon disulphide from the following data:

	$\Delta H_{\text{evap. m}}$ (cal mol^{-1})	Boiling point (°C)
Benzene	7363	80.2
CS_2	6400	46.3

11.6 The boiling point of a solution containing 25.6 g of a substance *X* per thousand grams of water is higher by 0.0514°C than the boiling point of pure water. Calculate the molar mass of *X*, if the ebullioscopic constant of water is 0.514 K/(mol kg^{-1}).

11.7 The molal elevation constant of benzene is 2.52 K kg mol^{-1}. A solution of some organic solute in benzene boils at a temperature 0.125° higher than benzene. What is the molality of the solution ?

11.8 (SI Units) Ten grams of sucrose are dissolved in 200 g of water. Calculate (a) the boiling point and (b) the freezing point of the solution (For water, $K_b = 0.512$ K/(mol kg^{-1}), $K_f = 1.86$ K/(mol kg^{-1}).

11.9 (SI Units) For carbon tetrachloride, $\Delta H_{\text{evap}\cdot m} = 30.0$ kJ mol^{-1} and $T_b = 350$ K. When 2 g of a substance *A* is dissolved in 5×10^{-2} kg of CCl_4, boiling point is raised by 0.526 K. Calculate the molar mass of substance *A*.

11.10 The freezing point of a solution of 0.321 g of naphthalene in 52.12 g of benzene is 5.155°C, while the freezing point of the pure solvent is 5.4°C. If the molecular depression of freezing point per 100 g of the solvent is 51.2 K/(mol per 100 g), calculate the molar mass of naphthalene.

11.11 A substance weighing 1.355 g was dissolved in 55 g of acetic acid. This produced a depression of 0.618°C in the freezing point. Calculate the molar mass of the dissolved substance. K_f for acetic acid = 38.5 K/(mol per 100 g).

11.12 (SI Units) Calculate the molar mass of a solute, 1 g of which, in solution depresses the freezing point of 50 g of benzene by 0.516 K ($K_f = 5.12$ K kg mol^{-1}).

11.13 The osmotic pressure of a solution containing 4 g of the solute per litre of the solution is 0.41 atm at 27°C. What is the molar mass of the solute ?

11.14 (SI Units) Calculate the osmotic pressure of a solution containing 10 g of cane sugar in 500 cm^3 at 300 K. Molar mass of cane sugar = 342.

11.15 The boiling point of an aqueous solution containing 6 g of the solute in 250 g of water is 100.052°C. What is its molar mass ? What will be its osmotic pressure at 27°C if molality is taken to be equal to molarity [$K_b = 0.52$ K kg mol^{-1}]?

11.16 Calculate the osmotic pressure, at 25°C, of a solution containing 0.342 g of sucrose (molar mass = 342), 0.36 g of glucose (molar mass = 180), and 0.03 g of urea (molar mass = 60) in 100 ml of solution.

11.17 (a) What is the osmotic pressure of a solution containing 1 mol dm^{-3} of solute at (i) 0°C and (ii) 25°C.

(b) What is the molarity of a solution with an osmotic pressure of 2 atmosphere at 25°C ? What volume of this solution would contain 1 mole solute ?

11.18 (SI Units) A solution containing 0.5 g of a polymer in 50 cm^3 of aqueous solution gave an osmotic pressure of 5.9×10^2 N m^{-2} at 298 K. What is the relative molar mass of the polymer ?

11.19 A solution is prepared by dissolving 36 g of glucose (molar mass = 180) in 1000 g of water. Calculate:

(a) Osmotic pressure at 25°C;

(b) Freezing point of the solution (K_f for water = 1.86 K/(mol kg^{-1})

(c) Boiling point of the solution (K_b for water = 0.511 K/(mol kg^{-1})

(d) Vapour pressure at 25°C, given that the vapour pressure of water at 25°C is 23.76 torr.

11.20 One litre of an aqueous solution contains, besides water, (a) 3 g of urea (b) 3.01×10^{22} molecules of sugar and (c) 0.04 moles of glucose. What is the osmotic pressure of the solution at 27°C ?

11.21 A decimolal solution of nitrous acid (HNO_2) freezes at 0.195° below the freezing point of water. Calculate the percentage ionization of nitrous acid (K_f for water = 1.86 K kg mol^{-1}).

11.22 A 2% solution of anhydrous $AlCl_3$ (molar mass = 133.5) is isotonic with a 6.5% solution of glucose. Calculate the percentage dissociation of $AlCl_3$.

11.23 The boiling point of a solution containing 6.5 g of $BaCl_2$ (molar mass = 208) in 200 g of water is 100.21°C. Calculate the apparent degree of dissociation of $BaCl_2$ at this concentration. The molal boiling point elevation constant for water is 0.514 K/(mol kg^{-1}).

11 24 (SI Units) An aqueous solution was found to have an osmotic pressure of 3.0×10^5 N m^{-2} at 298 K. What will be the freezing point of the solution (K_f for water = 1.86 K kg mol^{-1}) ?

11.25 Calculate the freezing point of a solution containing 6 g of phenol in 100 g of benzene if 80% of the phenol associates into $(C_6H_5OH)_2$ in benzene at this concentration. The freezing point of benzene is 5.5°C and K_f for benzene is 5.12 K kg mol^{-1}.

QUIZ QUESTIONS

Type A: Multiple Choice

11.26 Colligative properties depend upon the
(a) relative number of solute molecules in solution and the nature of the solvent
(b) relative number of solute molecules in solution and their nature
(c) relative number of solute molecules and the nature of solute and solvent
(d) relative number of solute molecules, irrespective of the nature of the solute and solvent

11.27 Which of the following is a colligative property ?
(a) viscosity
(b) surface tension
(c) osmotic pressure
(d) boiling point

11.28 Which of the following properties does not depend upon the number of solute particles ?
(a) elevation in boiling point
(b) osmotic pressure
(c) depression in freezing point
(d) boiling point of solvent.

11.29 If x_1 and x_2 are the mole fractions of the solvent and solute, respectively, $p°$ the vapour pressure of the pure solvent, and p the vapour pressure of the solvent above a given solution (solute being nonvolatile), then, according to Raoult's law,
(a) $p° = p\, x_1$
(b) $p = p°\,(1 - x_2)$
(c) $p - p° = x_1 - x_2$
(d) $\dfrac{p° - p}{p°} = \dfrac{x_1}{x_2}$

11.30 The temperature at which vapour pressure becomes equal to the external pressure is called the
(a) saturation point
(b) critical temperature
(c) elevation temperature
(d) boiling point

11.31 The freezing point of a solvent
(a) will increase on adding a solute
(b) will decrease on adding a solute
(c) will not change on adding a solute
(d) may increase or decrease on adding a solute, depending upon its nature

11.32 Iso-osmotic solutions are those which have the same
(a) osmotic pressure
(b) vapour pressure lowering
(c) molality
(d) ebullioscopic constant

11.33 In the Rast method for the determination of molecular masses, camphor has been used because of its
(a) high molal depression constant
(b) convenient melting point
(c) low molal depression constant
(d) easy availability

11.34 The osmotic pressure of a solution with a definite concentration
(a) varies directly as the volume and temperature
(b) varies inversely as the temperature
(c) varies inversely as the volume and directly as the temperature
(d) independent of temperature but varies inversely as the volume

11.35 The relative lowering of vapour pressure of a solution on the addition of a non-volatile solute
(a) is equal to the mole fraction of solute
(b) is equal to the sum of the mole fraction of solute and solvent
(c) depends upon the nature of the solute
(d) depends upon the nature of the solute and solvent

11.36 Which of the following aqueous solutions would exhibit abnormal osmotic pressure ?
(a) 0.1 M NaCl
(b) 0.1 M glucose
(c) 0 01 M glucose
(d) 0.1 M urea

11.37 Which of the following solutions would have the largest depression in freezing point ?
(a) 1% glucose
(b) 1% KCl
(c) 1% $BaCl_2$
(d) 1% sucrose

11.38 Which of the following methods is used for the determination of osmotic pressure ?
(a) Cottrell method
(b) Landsberger's method
(c) Beckmann's method
(d) Berkeley and Hartley's method

11.39 The molar mass of a solute in a solvent can be calculated from the elevation in boiling point using the relation

(a) $\dfrac{K_b \times 1000 \times \text{wt. of solvent}}{\Delta T_b \times \text{wt. of solute}}$

(b) $\dfrac{1000 \times \text{wt. of solute}}{K_b \times \Delta T_b \times \text{wt. of solvent}}$

(c) $\dfrac{1000 \times K_b \times \text{wt. of solute}}{\Delta T_b \times \text{wt. of solvent}}$

(d) $\dfrac{\Delta T_b \times K_b \times \text{wt. of solute}}{1000 \times \text{wt. of solvent}}$

11.40 The flow of a solvent into a solution when the two are separated by a semi-permeable membrane is called
(a) diffusion
(b) osmosis
(c) effusion
(d) mixing

11.41 Sea water is converted into fresh water based upon the phenomenon of
(a) plasmolysis
(b) sedimentation
(c) reverse osmosis
(d) diffusion

11.42 In a dilute aqueous solution the relative lowering in vapour pressure $(\Delta p/p^\circ)$ is related to osmotic pressure (π) by the relation

(a) $\Delta p/p^\circ = \pi$

(b) $\dfrac{\Delta p}{p^\circ} = \pi RT$

(c) $\dfrac{\Delta p}{p^\circ} = \dfrac{\pi V}{RT}$

(d) $\dfrac{\Delta p}{p^\circ} = \dfrac{\pi RT}{V}$

11.43 By adding a non-volatile solute to a solvent, the boiling point of the solvent

(a) will increase

(b) will decrease

(c) will not change

(d) may increase or decrease

11.44 At the same temperature, 0.1 M solution of urea is isotonic with

(a) 0.1 M glucose solution

(b) 0.1 M NaCl solution

(c) 0.05 M urea solution

(d) 0.1 M $BaCl_2$ solution

11.45 If ΔT_b is the elevation in boiling point for the electrolyte and ΔT_b° for the non-electrolyte of the same concentration, then Van't Hoff factor i is

(a) $\Delta T_b \times \Delta T_b^\circ$

(b) $\Delta T_b^\circ / \Delta T_b$

(c) $\dfrac{\Delta T_b - \Delta T_b^\circ}{2}$

(d) $\Delta T_b / \Delta T_b^\circ$

11.46 If in a solvent, n simple molecules of solute combine to form an associated molecule, x is the degree of association, then Van't Hoff factor is equal to

(a) $\dfrac{1}{1 - nx}$

(b) $\dfrac{1 - x + nx}{1}$

(c) $\dfrac{1 - x + \dfrac{x}{n}}{1}$

(d) $\dfrac{\dfrac{x}{n} - 1 + x}{1}$

11.47 Which of the following will have the highest boiling point at one atmospheric pressure ?

(a) 0.1 M solution of common salt

(b) 0.1 M solution of sucrose

(c) 0.1 M solution of barium chloride

(d) 0.1 M solution of potassium chloride

11.48 In a 0.5% aqueous solution of common salt (degree of dissociation$=x$), the observed molar mass obtained by the freezing point-depression method will be related to the actual molar mass (M) as

(a) $M(1 - x)$

(b) $M/(1 + x)$

(c) $M(1 + x)$

(d) $M/2x$

11.49 Which of the following effects is not observed when a non-volatile solute is added to a solvent?

(a) decrease in vapour pressure

(b) lowering of freezing point

(c) elevation of boiling point

(d) increase of freezing point

11.50 For a solvent with heat of vaporisation per gram, h_{evap} and normal boiling point T, the ebullioscopic constant, K_b (K mol⁻¹ kg) is

(a) $\dfrac{RT^2}{h_{evap} \times 1000}$ (b) $\dfrac{h_{evap} \times 1000}{RT^2}$

(c) $\dfrac{1000\,RT^2}{h_{evap}}$ (d) $\dfrac{R \times 1000 \times h_{evap}}{T}$

11.51 Which of the following aqueous solutions has osmotic pressure nearest to that of an equimolar solution of $K_4[Fe(CN)_6]$?

(a) $C_{12}H_{22}O_{11}$ (b) Na_2SO_4

(c) $Al_2(SO_4)_3$ (d) $BaCl_2$

11.52 Which of the following compounds in their aqueous solutions (1 M, assume all salts to be 90% dissociated) will have the maximum osmotic pressure?

(a) KCl (b) $BaCl_2$

(c) $FeCl_3$ (d) $(NH_4)_3PO_4$

11.53 Consider a 0.1 M solution of two solutes *A* and *B*. *A* behaves as a non-electrolyte while 80% of *B* dimerises. Which of the following statements is correct regarding these solutions:

(a) The boiling point of solution *A* will be less than that of *B*.

(b) The osmotic pressure of solution *B* will be more than that of *A*.

(c) The freezing point of solution of *A* will be less than that of *B*.

(d) Boiling points of both solutions will be the same.

11.54 At a constant temperature, with increase in concentration of solute, the osmotic pressure of a solution

(a) increases

(b) decreases

(c) remains constant

(d) nothing certain

11.55 For a solution containing three solutes, *A*, *B* and *C* having concentrations m_A, m_B and m_C, respectively, the ratio between elevation of boiling point and depression of freezing point will be

(a) $\dfrac{K_b}{K_f}(m_A + m_B + m_C)$

(b) $\dfrac{K_f}{K_b}(1 - m_A - m_B - m_C)$

(c) $\dfrac{K_f}{K_b}$

(d) $\dfrac{K_b}{K_f}$

Type B: Multiple Choice (Numerical Problems)

11.56 The vapour pressure of water at 20°C is 17.5 torr. The lowering of vapour pressure of a glucose solution is 0.0525 torr. The mole fraction of water is

(a) 0.003 (b) 0.9970

(c) 17.497 (d) 17.4475

11.57 A solution of a non-volatile solute in benzene boiled at a temperature 0.126°C higher than benzene. How many moles of solute are present in 100 g of benzene (molal elevation constant of benzene=2.52 K kg/mol)?

(a) 0.05 (b) $2.52 \times 0.126/100$

(c) 0.005 (d) 5.0

11.58 A solution containing 1 g of solute per 100 g of benzene freezes at 0.4° lower than pure benzene. Calculate the molar mass of the solute (K_f for benzene =5.12 K kg mol⁻¹).

(a) 204.8 (b) 128

(c) 1280 (d) 20.48

11.59 An aqueous solution freezes at $-0.186°C$. The elevation in boiling point ($K_f = 1.86°$, $K_b = 0.512°$) is
(a) 0.186 (b) 0.512
(c) 0.0512 (d) 0.512/1.86

11.60 The osmotic pressure of a solution containing 4 g of solute per litre of solution is 0.4 atm at 27°C. The molar mass of the solute is ($R = 0.082$ *l* atm mol^{-1} K^{-1})
(a) 246 (b) 984
(c) 24.6 (d) 98.4

11.61 Water boils at 100°C. What will be the boiling point of a solution containing 6 g of glucose (mol. mass = 180) per 1000 g of water. Molal elevation constant for water = 0.513 K mol^{-1} kg.
(a) 101.539 (b) 100.017
(c) 100.153 (d) 99.983

11.62 Calculate the osmotic pressure of 6% urea (molar mass = 60) ($R = 0.082$ *l* atm/mole-degree)
(a) 22.4 atm (b) 24.6 atm
(c) 2.46 atm (d) 27.3 atm

11.63 Morse and Frazer observed that a solution of 20 g of a compound per litre gave an osmotic pressure of 3 atm at 27°C. The molar mass of the compound is ($R = 0.082$ *l* atm deg^{-1} mol^{-1})
(a) 492 (b) 369
(c) 164 (d) 496

11.64 The molar mass of 0.5% sodium chloride has been found to be 30. What is the apparent degree of dissociation of NaCl at this concentration?
(a) 0.95 (b) 0.475
(c) 0.565 (d) 0.966

11.65 Phenol associates, in benzene, to form double molecules. By the freezing point depression method, the Van't Hoff factor has been found to be 0.54. To what degree is phenol associated?
(a) 0.46 (b) 0.54
(c) 0.98 (d) 0.92

Type C: True or False

11.66 The molar mass of potassium chloride, determined by the osmotic pressure method, will be higher than the theoretical value.

11.67 A semi-permeable membrane allows only solute molecules to pass through it.

11.68 The boiling point of a solvent will increase on adding a non-volatile solute.

11.69 The vapour pressure of a solution is higher than the vapour pressure of the solvent.

11.70 The osmotic pressure of a dilute solution is the same as the pressure which the solution would exert if it existed in the gaseous state and occupied the volume of the solution.

11.71 Relative lowering of vapour pressure is independent of both the nature of the solute and solvent.

11.72 There will be no net flow of solvent when two iso-osmotic solutions are separated by a semipermeable membrane.

11.73 The osmotic pressure of sodium chloride solution will be more than that of a solution of the same concentration of glucose.

11.74 Osmosis is due to the flow of solvent from a low (solvent) to high chemical potential (solution).

11.75 Osmotic pressure is directly proportional to temperature.

11.76 If a solute associates in a solvent the depression in its freezing point will be more than the value when it does not associate.

11.77 The process of osmosis in case of animal and vegetable cells is called plasmolysis.

11.78 The phenomenon of the movement of particles of solute from a greater to a lesser concentrated solution is called diffusion.

11.79 Vapour pressure is a colligative property.

11.80 In case of solutes which dissociate in a solvent, the observed molar mass will always be less than its theoretical value.

Type D: Fill in the blanks

11.81 The relative lowering of vapour pressure is equal to the mole fraction of ————.

11.82 Solutions which have the same osmotic pressures are called ————.

11.83 The boiling point of a solution is always ———— than the boiling point of the pure solvent, regardless of atmospheric pressure.

11.84 The osmotic pressure of a solution is directly proportional to ———— and inversely proportional to ————.

11.85 The ratio of the theoretical molar mass to the observed molar mass is called ————.

11.86 The relative lowering in vapour pressure is ———— proportional to osmotic pressure.

11.87 The temperature at which the vapour pressure becomes equal to the atmospheric pressure is called ————.

11.88 Benzoic acid dimerizes in water. The freezing point of its solution will be ———— than 0°C.

11.89 The Cottrell method is used for measurement of the ————.

11.90 The process of conversion of sea water into fresh water is based on ————.

ANSWERS

Numerical Problems

11.1 3.132×10^3 N m^{-2} *11.2* 60.56 *11.3* 48.2 *11.4* 66.6 *11.5* 2.62, 2.40 *11.6* 256 *11.7* 0.0496 mol kg^{-1} *11.8* (a) 373.15 (b) 272.46 *11.9* 397.7 *11.10* 128.7 *11.11* 153.5 *11.12* 198.4 *11.13* 240 *11.14* 1.46×10^5 N m^{-2} *11.15* 240 *11.16* 1.95 atm *11.17* (a) 22.4 atm, 24.4 atm (b) 0.089 M, 11.2 *l* *11.18* 4×10^4 *11.19* (i) 0.049 atm, (ii) −3.72° (iii) 101.028°C (iv) 22.9 torr *11.20* 3.44 atm *11.21* 4.8% *11.22* 47% *11.23* 81% *11.24* 272.775 K *11.25* 3.55°C.

Quiz Questions

11.26 (a) *11.27* (c) *11.28* (d) *11.29* (b) *11.30* (d) *11.31* (b) *11.32* (a) *11.33* (a) *11.34* (c) *11.35* (a) *11.36* (a) *11.37* (c) *11.38* (d) *11.39* (c) *11.40* (b) *11.41* (c) *11.42* (c) *11.43* (a) *11.44* (a) *11.45* (d) *11.46* (c) *11.47* (c) *11.48* (b) *11.49* (d) *11.50* (a) *11.51* (c) *11.52* (d) *11.53* (c) *11.54* (a) *11.55* (d) *11.56* (b) *11.57* (c) *11.58* (b) *11.59* (c) *11.60* (a) *11.61* (b) *11.62* (b) *11.63* (c) *11.64* (a) *11.65* (d) *11.66* True *11.67* False: Semipermeable membrane allows only solvent molecules to pass *11.68* True *11.69* False *11.70* True *11.71* True *11.72* True *11.73* True *11.74* False *11.75* True *11.76* False *11.77* False *11.78* True *11.79* False *11.80* True *11.81* solute *11.82* iso-osmotic *11.83* more *11.84* temperature, volume *11.85* Van't Hoff factor *11.86* directly *11.87* boiling point *11.88* less *11.89* elevation in boiling point *11.90* reverse osmosis.

12

Phase Equilibria and Phase Rule

The study of physical equilibria between different states of matter, consisting of one or more chemical species, forms the subject matter of phase equilibria. It involves three important terms: phase, component and degree of freedom. The relation between the number of phases, components and degrees of freedom is known as the phase rule.

12.1 PHASE

A phase is defined as the homogeneous, physically distinct and mechanically separable part of the system which is separated from other parts by definite boundaries. The number of phases P in a heterogeneous system is the number of such homogeneous parts.

Gaseous Phase

All gases are completely miscible.* Therefore, even if a system contains a number of different gases or vapours, it can have only one phase.

Liquid Phase

The number of liquid phases depends on the number of liquids and their mutual solubilities:

(a) Two or more miscible liquids constitute one phase, e.g. water and alcohol.

(b) Immiscible liquids constitute different phases, e.g. water and benzene exist in two phases.

(c) For partially miscible liquids, the number of phases will depend on the composition, e.g. a mixture of water and ether exists as one phase at extreme compositions, but at intermediate compositions the system consists of two phases.

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*Under normal pressure, all gases are completely miscible. However, it has been observed that at very high pressures, gases with weak intermolecular forces show gas-gas immiscibility (Refer G.M. Schneider, *Adv. Chem. Phys.*, 1970, **17**, 1).

Solid Phase

The number of solid phases in a system is equal to the number of solids present in the system. The allotropic forms of a substance are considered different solids and, hence, form different phases. However, a solid solution or mixed crystals (considered as one solid dissolved in another solid) must be regarded as a single phase, e.g. β-naphthol and naphthalene, *p*-dichlorobenzene and *p*-dibromobenzene (solid solutions) and mixed crystals of NaCl and KCl exist as single phases.

12.2 COMPONENTS

The number of components *C* is defined as the smallest number of independent chemical constituents required to express the composition of each phase in the system.

It may be noted that the number of components is not equal to the total number of molecular species present in the system, but is the minimum number of molecular species in terms of which the composition of all the phases may be expressed. For example,

(a) The water system consisting of three phases,

$$\text{ice(s)} \rightleftharpoons \text{water(l)} \rightleftharpoons \text{vapour(g)}$$

is a one-component system because all three phases are fully described in terms of H_2O. The species H^+ and OH^- are also present, but their concentrations are related to that of H_2O through the dissociation constant.

(b) The sulphur system is a one-component system although there may be a combination of rhombic, monoclinic, liquid and vapour phases.

(c) The system

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

is a two-component system because the composition of each phase in the system can be described in terms of any two of the constituents.

12.3 DEGREE OF FREEDOM OR VARIANCE

The number of degrees of freedom or variance *F* is the minimum number of independent variables required to characterize the system completely. These are intensive variables like temperature, pressure and concentration of various components in different phases. They characterize different phases and hence the system itself. However, the number of variables means the minimum number of independent variables which are necessary to define each phase. Their choice depends on our convenience.

12.4 EQUILIBRIUM IN A MULTI-PHASE SYSTEM

Equilibrium in a multi-phase system implies that the properties of none of the phases change with time. This requires the following conditions:

(a) There should be equality of temperature of all the phases so that there is no net flow of heat from one phase to the other (thermal equilibrium).

(b) All phases should be under the same pressure so that there is no hydrodynamic flow of material from high pressure to low pressure regions (mechanical equilibrium).

(c) The chemical potential of each component is the same for all the phases so that there is no net flow of any one component from one phase to another (composition equilibrium).

12.5 PHASE RULE

The relation between the number of phases P, the number of components C, and the number of degrees of freedom F was first deduced by J. Willard Gibbs (1878) and is known as the phase rule. It is expressed as

$$P + F = C + 2$$

Deduction of Phase Rule

It was deduced by counting the total number of intensive variables of the system required for describing all the phases, and subtracting from these the number of relations which may exist between the values of these variables in different phases.

In addition to variables p and T for the entire system, the composition of each phase is described by $(C-1)$ concentrations. For P phases, the total number of concentration variables are $P(C-1)$. Thus, the total number of variables for all the phases are

$$P(C-1) + 2$$

Now, the chemical potential of a component is the same in all phases under equilibrium. Therefore, for a system of P phases, for each component there are $(P-1)$ relations equating the chemical potential in each phase. For C components, the number of such relations are $C(P-1)$.

Therefore, the minimum number of variables required, i.e. degrees of freedom F, is

$$F = P(C-1) + 2 - C(P-1)$$

or $$P+F = C+2$$

EXAMPLE 12.1 Calculate the number of phases (P), components (C) and degrees of freedom (F) for the following systems:

(a) Ammonium chloride in equilibrium with ammonia and hydrochloric acid

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

(b) ammonium chloride in equilibrium with ammonia and hydrochloric acid with a certain amount of hydrochloric acid initially present in the system.

(c) Magnesium carbonate in equilibrium with its decomposition products.

$$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$$

Solution (a) Number of phases = 2
Number of components = 1

It is a one-component system because the concentration of NH_3 is always equal to the concentration of HCl in the vapour phase.

By phase rule,

$$P + F = C + 2$$

$$2 + F = 1+2 \quad \text{or } F=1$$

(b) Number of phases = 2
Number of components = 2

It is a two-component system because the concentration of NH_3 is not always equal to the concentration of HCl in the vapour phase.

$$P + F = C + 2$$

$$2 + F = 2+2 \quad \text{or } F = 2$$

(c) Number of phases = 3 (two solid phases and one gaseous phase)
Number of components = 2

By defining the composition of two species ($MgCO_3$, MgO), that of the third is automatically defined.

$$P + F = C + 2$$

$$3 + F = 2+2 \quad \text{or } F = 1$$

12.6 PHASE EQUILIBRIA IN ONE-COMPONENT SYSTEMS

Single-Phase System

A pure substance existing in a single phase (gas, liquid and solid) will have $F = 2$ ($P = 1$, $C = 1$). Thus, it requires two variables such as T, p for describing its state.

Two-Phase Systems

In the case of systems consisting of two phases, 1 and 2 (e.g. vapour and liquid, vapour and solid, liquid and solid or solid and solid), a relation can be defined:

$$\frac{pd}{dT} = \frac{\Delta H_{\text{transition}}}{T\,(V_2 - V_1)}$$

where $\Delta H_{\text{transition}}$ is the enthalpy of transition for the conversion of one mole of the substance from phase 1 to phase 2 and p, T and V are pressure, temperature and volume. This is a general equation.

(a) *Liquid-Vapour Equilibrium.* Here

$$\Delta H_{\text{transition}} = \Delta H_{\text{evap}}$$

and

$$V_2 - V_1 = V_{\text{vap}} - V_{\text{liq}}$$

$$\frac{dp}{dT}=\frac{\Delta H_{\text{evap}}}{T(V_{\text{vap}}-V_{\text{liq}})}$$

This equation is called the Clausius-Clapeyron equation. It can be simplified if the volume of liquid is negligible in comparison to the volume of vapour so that $V_{\text{vap}}-V_{\text{liq}}\approx V_{\text{vap}}$ and vapours behave as ideal gases so that

$$V_{\text{vap}}=\frac{RT}{p}$$

or $$\frac{dp}{dT}=\frac{\Delta H_{\text{evap}}\times p}{RT^2}$$

and $$\log\frac{p_2}{p_1}=\frac{\Delta H_{\text{evap}}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

(b) *Solid-Vapour Equilibrium*

For solid-vapour equilibrium, $\Delta H_{\text{transition}}=\Delta H_{\text{sub}}$

$$\frac{dp}{dT}=\frac{1}{T}\left[\frac{\Delta H_{\text{sub}}}{V_{\text{vap}}-V_{\text{solid}}}\right]$$

For $V_{\text{vap}}\gg V_{\text{solid}}$ and vapours behaving ideally,

$$\frac{dp}{dT}=\frac{\Delta H_{\text{sub}}\times p}{RT^2}$$

and $$\log\frac{p_2}{p_1}=\frac{\Delta H_{\text{sub}}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

(c) *Solid-Liquid Equilibrium*

Here $\Delta H_{\text{transition}}=\Delta H_{\text{fus}}$

$$\frac{dp}{dT}=\frac{\Delta H_{\text{fus}}}{T(V_{\text{liquid}}-V_{\text{solid}})}$$

or $$\frac{dp}{dT}=\frac{\Delta H_{\text{fus}}}{T\Delta V_{\text{fus}}}\qquad\left[\because\ \Delta V_{\text{fus}}=V_{\text{liquid}}-V_{\text{solid}}\right]$$

(d) *Solid-Solid Equilibrium*

If a substance changes from one crystalline form to another,

$$\frac{dp}{dT}=\frac{\Delta H_{\text{transition}}}{T(V_{\text{II}}-V_{\text{I}})}$$

where V_{I} and V_{II} are volumes in the two crystalline forms.

EXAMPLE 12.2 The atmospheric pressure at Shimla on a particular day is 610 torr. At what temperature does water boil in Shimla on that day ($\Delta H_{\text{evap}}=40.67$ kJ mol^{-1})?

Solution We have

$$\log\frac{p_2}{p_1}=\frac{\Delta H_{\text{evap},\,m}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$T_1=273+100=373,\quad p_1=760$ torr

$p_2=610$ torr, $\quad T_2=?$

$\Delta H_{\text{evap},\,m}=40.67$ kJ mol^{-1}

$$\log\frac{610}{760}=\frac{40.67\times10^3}{2.303\times8.314}\left[\frac{1}{373}-\frac{1}{T_2}\right]$$

$$T_2=366.8\text{ K}=93.7^\circ\text{C}$$

EXAMPLE 12.3 The vapour pressure of liquid 2, 2, 4-trimethylpentane at 20.7 and 29.1°C are 40 and 60 torr, respectively. Estimate the enthalpy of vaporization of this compound.

Solution

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{evap},\,m}}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$T_1 = 273+20.7 = 293.7$ K, $\quad p_1 = 40$ torr

$T_2 = 273+29.1 = 302.1$ K, $\quad p_2 = 60$ torr

$$\log \frac{60}{40} = \frac{\Delta H_{\text{evap},\,m}}{2.303\times 8.314}\left[\frac{1}{293.7}-\frac{1}{302.1}\right]$$

$$0.1761 = \frac{\Delta H_{\text{evap},\,m}}{2.303\times 8.314}\left[\frac{302.1-293.7}{293.7\times 302.1}\right]$$

$$\Delta H_{\text{evap},\,m} = 35.6 \text{ kJ mol}^{-1}$$

EXAMPLE 12.4 The latent heat of fusion of water is 1440 cal mol^{-1}. What will be its melting point at 5 atm if the densities of water and ice are 1 and 0.9 g cm^{-3}, respectively?

Solution $\quad \dfrac{dT}{dp} = \dfrac{T(V_{\text{liq}}-V_{\text{solid}})}{\Delta H_{\text{fus}}}$

$\Delta H_{\text{fus}} = 1440$ cal mol^{-1}, $V_{\text{liq}} = \dfrac{18}{1.0}$ cm^3, $V_{\text{solid}} = \dfrac{18}{0.9} = 20$ cm^3

Melting point of water at 1 atm = 0°C = 273.15 K

$$\frac{dT}{dp} = \frac{273.15(18-20)}{1440}\ \frac{\text{cm}^3\text{K}}{\text{cal}}$$

$$= \frac{273.15 \text{ K} \times (-2\times 10^{-3} l)}{1440 \times \left(\dfrac{0.082}{1.987}\right) \text{atm } l}$$

$$= -0.0092 \text{ K atm}^{-1}$$

At 5 atm, $\quad dp = 5-1 = 4$ atm

$dT = -\,0.0092 \times 4 = -0.0368$ K

Melting point at 5 atm $= 273.15 - 0.0368 = 272.1132$ K

EXAMPLE 12.5 (SI Units) The molar volumes of water and ice are 18.05×10^{-3} dm^3 mol^{-1} and 19.64×10^{-3} dm^3 mol^{-1}, respectively. Calculate the change in freezing point of ice with 1.01×10^3 k Nm^{-2} increase in pressure. ($\Delta H_{\text{fus}} = 6.01$ kJ mol^{-1}).

Solution $\quad \dfrac{dp}{dT} = \dfrac{\Delta H_{\text{fus}}}{T(V_{\text{liq}}-V_{\text{solid}})}$

$\Delta H_{\text{fus}} = 6.01 \times 10^3$ J mol^{-1}

$T = 273$ K

$V_1 = 18.05 \times 10^{-3}$ dm^3 mol^{-1}, V_{solid}

$= 19.64 \times 10^{-3}$ dm^3 mol^{-1}

$$\frac{dp}{dT} = \frac{6.01 \times 10^3 \text{ J mol}^{-1}}{(273 \text{ K}) \times [18.05 \times 10^{-3} - 19.64 \times 10^{-3}] \text{ dm}^3 \text{ mol}^{-1}}$$

$$= -13846 \text{ J K}^{-1} \text{ dm}^{-3} = -\ 13846 \text{ k Nm}^{-2} \text{ K}^{-1}$$

Now, $dP = 1.01 \times 10^3 \text{ k Nm}^{-2}$

$$dT = \frac{1.01 \times 10^3 \text{ k Nm}^{-2}}{-13846 \text{ k Nm}^{-2} \text{ K}^{-1}} = -\,0.073 \text{ K}$$

Thus, temperature decreases by 0.073 K for 1.01×10^3 k N m^{-2} increase in pressure.

Solid–Liquid Equilibria and Cooling Curves

Solid-liquid equilibria are studied by the thermal analysis method. In this method, cooling curves (temperature–time) of the melts of various compositions are recorded, which help to recognise the separation of the solid by lowering or arresting the rate of cooling. The cooling curve of a pure (one-component) substance is shown in Fig. 12.1(a). Line *ab* gives the rate of cooling of the liquid, point *b* represents the beginning of freezing. The temperature remains constant until all the liquid is converted into solid, as indicated by the horizontal line *bc*. In other words, *bc* represents the solid–liquid equilibrium. Line *cd* gives the rate of cooling of the solid. In many cases, super-cooling takes place.

Figure 12.1(b) gives the cooling curve for a solution or a liquid system of two components. Line *ab* gives the cooling of the liquid solution, point *b* represents the first break (arrest point) when one component starts crystallising out. Line *bc* represents the variation of freezing point of the solution and point *c* gives the second break when a mixture of the two components (eutectic mixture) starts separating. After complete solidification of the mixture (point *d*), the line *de* gives the cooling of the solid mixture.

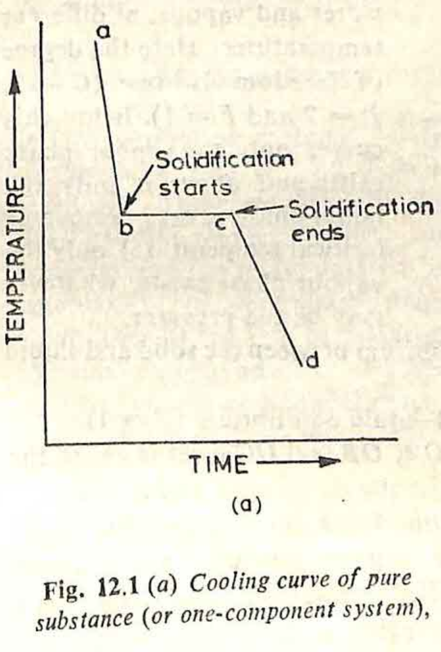


Fig. 12.1 (*a*) *Cooling curve of pure substance (or one-component system)*,

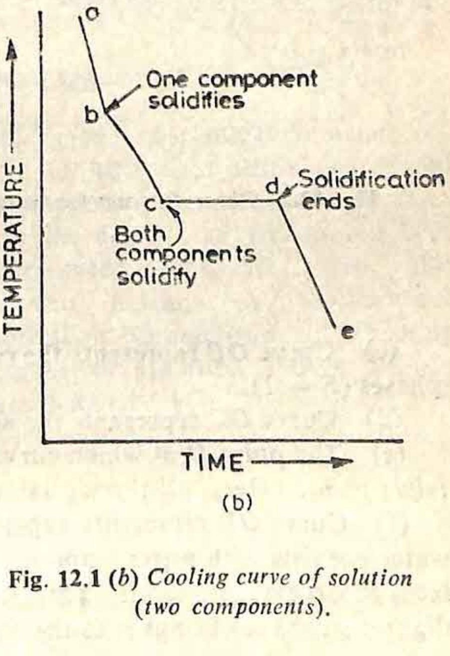


Fig. 12.1 (*b*) *Cooling curve of solution (two components)*.

To construct phase diagrams, several mixtures of different compositions are prepared and cooling curves for each composition are drawn. Then a graph is plotted between temperatures of the first and second break and the composition. The curve for the first break (b) versus composition is called the *liquidus curve* (pure solid and solution), whereas the curve for the second break (c) versus composition is called the *solidus curve*. These cooling curves help in drawing the phase diagrams.

12.7 PHASE DIAGRAMS

A phase diagram is the sum total of the descriptions of the behaviour of phases under equilibrium, over a range of variables. Some selected phase diagrams are briefly discussed below.

12.8 PHASE DIAGRAMS OF ONE-COMPONENT SYSTEMS

Water System

The phase diagram of water is shown in Fig. 12.2.

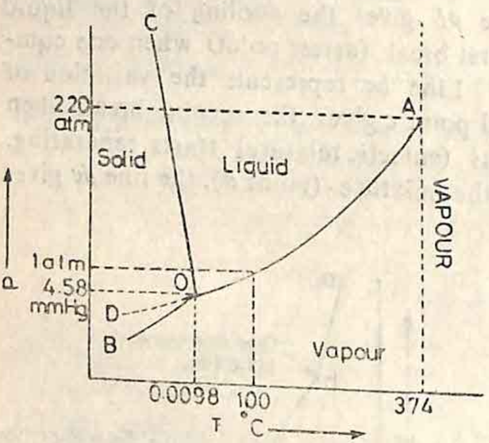


Fig. 12.2 *Phase diagram for water.*

(a) Curve OA starts from O, the freezing point of water (0.0098°C under 4.58 torr pressure), and ends at A, the critical temperature (374°C) and critical pressure (220 atm).

(b) Curve OA represents the equilibrium between liquid water and vapour, at different temperatures. Here the degree of freedom is one ($C = 1$, $P = 2$ and $F = 1$). Below this curve, only the vapour phase exists and above it only the liquid phase exists. Above A (critical temperature) only the vapour phase exists, whatever may be the pressure.

(c) Curve OB represents the equilibrium between the solid and liquid phases ($F = 1$).

(d) Curve OC represents the solid–liquid equilibrium ($F = 1$).

(e) The point O at which curves OA, OB and OC meet is called the *triple point*. Here, all three phases exist simultaneously and $F = 0$.

(f) Curve OD represents supercooling for water. Along this curve, water coexists with water vapour, and vapour pressures are different from those over the solid. This is called *metastable equilibrium* as a slight disturbance brings it to the stable region of the phase diagram.

Sulphur System

Sulphur can exist as rhombic, monoclinic, liquid and vapour. The phase diagram of sulphur is shown in Fig. 12.3.

(a) *AB* is the vapour pressure curve of rhombic sulphur and represents equilibrium between rhombic sulphur and the vapour ($F = 1$).

(b) At point *B*, rhombic sulphur is converted into monoclinic sulphur. Curve *BC* represents the vapour pressure curve of monoclinic sulphur

$(S_M \rightleftharpoons S_V)$

(c) Curve *CD* represents the vapour pressure curve of liquid sulphur ($S_L \rightleftharpoons S_V$).

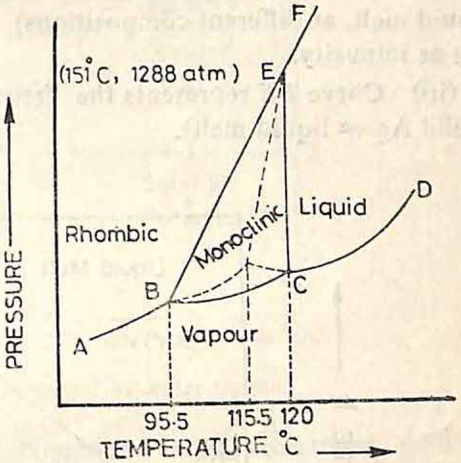


Fig. 12.3 *Phase diagram of sulphur.*

(d) *BE* represents the effect of pressure on the transition temperature of rhombic sulphur into monoclinic ($S_R \rightleftharpoons S_M$).

(e) *CE* represents the melting point curve of monoclinic sulphur and the effect of pressure on the melting point ($S_M \rightleftharpoons S_L$).

(f) $B(S_M, S_R, S_V)$, $C(S_M, S_L, S_V)$ and $E(S_M, S_R, S_L)$ are triple points where three phases coexist simultaneously.

(g) If rhombic sulphur is heated rapidly or liquid sulphur is cooled rapidly, each is converted directly to the other without passing through the monoclinic sulphur stage. This represents metastable equilibrium.

12.9 PHASE DIAGRAMS OF TWO-COMPONENT SYSTEMS

In two-component systems if only one phase is present, then, according to the phase rule ($C = 2$, $P = 1$, $F = 3$), there are three degrees of freedom. These are normally chosen as pressure, temperature and composition. To avoid difficulty, one of the degrees of freedom is kept constant and the phase diagram is represented by the other two. The complexity of the phase diagram also depends on the mutual solubilities of the two components and their capabilities of forming chemical compounds of varying degrees of stability. Some simple varieties of two-component systems are discussed here.

Type A

The components are completely miscible with one another and do not form any compound.

Lead-Silver System

The phase diagram is shown in Fig. 12.4 and the areas and curves are marked.

(i) *A* and *B* represent melting or freezing points of pure Pb(327°C) and Ag(961°C), respectively.

(ii) Curve *AE* represents the freezing point of lead (solid lead $\rightleftharpoons$ liquid melt, at different compositions). Freezing point is lowered due to Ag as impurity.

(iii) Curve *BE* represents the freezing point of silver from the melt (solid Ag $\rightleftharpoons$ liquid melt).

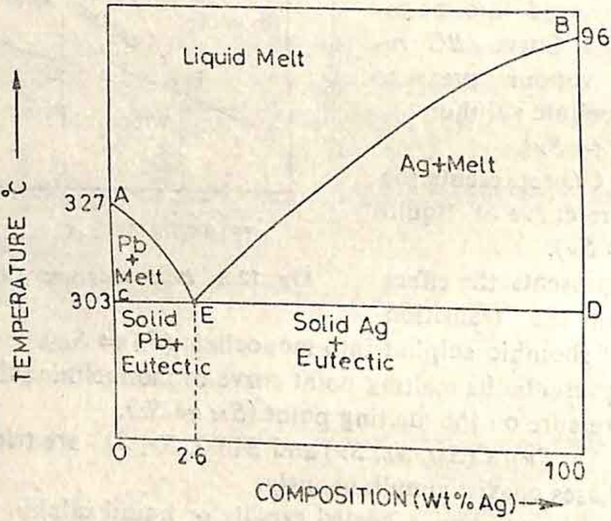


Fig. 12.4 *Phase diagram for lead–silver system.*

(iv) Point *E* is called the *eutectic point* where the composition of the melt is the same as that of the solid (mixture of Pb and Ag). Thus, it behaves as a pure compound and all the melt will freeze out at constant temperature. For each system, the eutectic has a characteristic composition. The temperature corresponding to this point (303°C) is called the *eutectic temperature*, and the composition (2.6% Ag) is called the *eutectic composition*. It changes with pressure and hence does not represent any chemical compound.

Potassium Iodide-Water System

The phase diagram with complete labelling is shown in Fig. 12.5.

(i) Here *E* is the eutectic point (−23°C). For the salt-water mixture, it is called the cryohydric point and the eutectic itself is called the *cryohydrate.*

(ii) Curve *EB* is incomplete as, at a given vapour pressure of water, all of it may be converted into a vapour state much before the temperature reaches the melting point of KI.

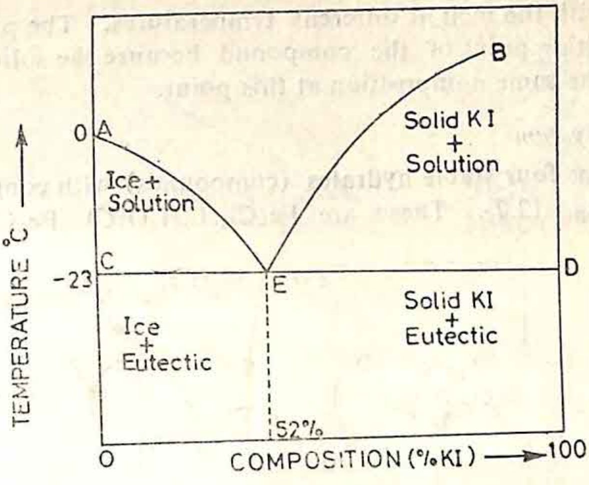


Fig. 12.5 *Phase diagram of KI–water system.*

Type B

The two components form a solid compound with congruent melting points

The stable compound melts at a constant temperature into a liquid of the same composition. Such compounds are said to have *congruent melting* points.

Zinc-magnesium System

In this system, a compound of composition $Mg(Zn)_2$ is formed (Fig. 12.6).

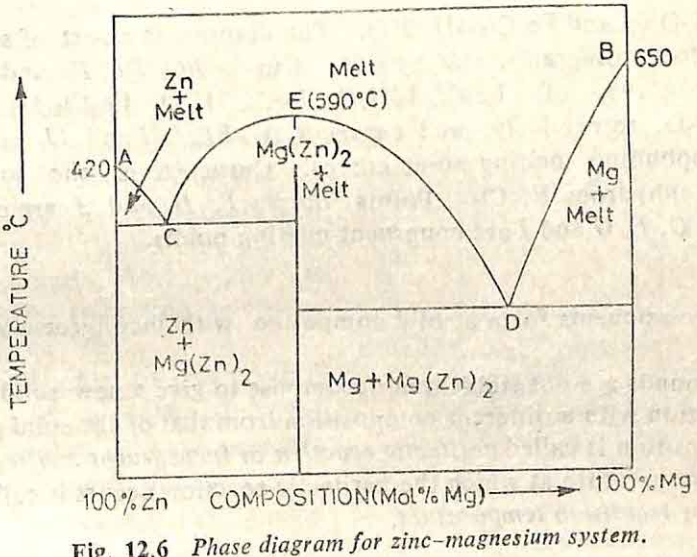


Fig. 12.6 *Phase diagram for zinc–magnesium system.*

(i) Along *AC* zinc is in equilibrium with the melt, and along *BD* Mg is in equilibrium with the melt. At *C* the melt is in equilibrium with Zn and the new compound, and at *D* the melt is in equilibrium with Mg and the new compound. Points *C* and *D* represent two eutectics and generally have different temperatures. Along *CED* the new compound is in equilibrium with the melt at different temperatures. The point *E* is the congruent melting point of the compound because the solid and liquid phases have the same composition at this point.

$FeCl_3$–Water System

This system has four stable hydrates (compounds) with congruent melting point (Fig. 12.7). These are $Fe_2Cl_6.12H_2O$(*C*), $Fe_2Cl_6.7H_2O$(*E*), $Fe_2Cl_6.5H_2O$(*G*) and $Fe_2Cl_6.4H_2O$(*I*). The diagram is a sort of series of simple eutectic diagrams, side by side. Curves *BC*, *DE*, *FG* and *HI* are solubility curves of $Fe_2Cl_6.12H_2O$, $FeCl_6.7H_2O$, $Fe_2Cl_6.5H_2O$ and $Fe_2Cl_6.4H_2O$, respectively, and curves *CD*, *EF*, *GH* and *IJ* represent the corresponding melting point curves. Curve *JK* is the solubility curve of anhydrous Fe_2Cl_6. Points *B*, *D*, *F*, *H* and *J* are eutectic points and *C*, *E*, *G* and *I* are congruent melting points.

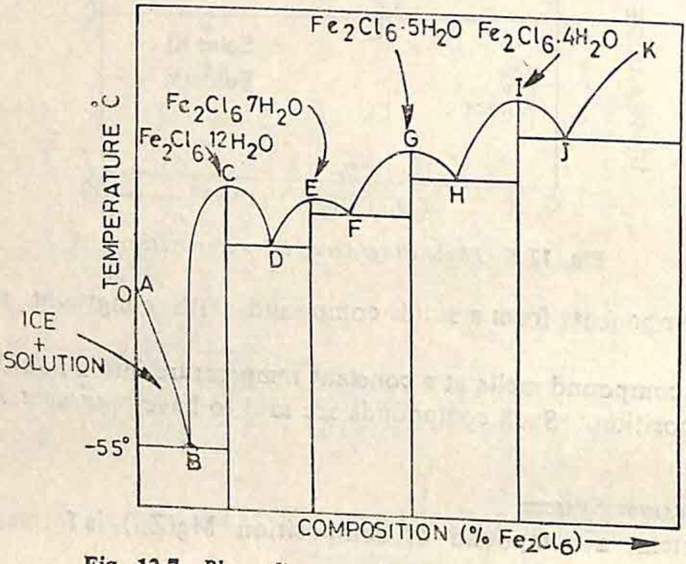


Fig. 12.7 *Phase diagram of $FeCl_3$–water system.*

Type C

The two components form a solid compound with incongruent melting point.

The compounds are not stable and decompose to give a new solid phase and a solution with a different composition from that of the solid phases. Such a transition is called *peritectic reaction* or *incongruent melting*. The constant temperature at which the peritectic reaction occurs is called the *peritectic* or *transition temperature*.

CaF_2–$CaCl_2$ System

The phase diagram for the CaF_2–$CaCl_2$ system is shown in Fig. 12.8.

(i) *AD* and *BC* represent CaF_2 and $CaCl_2$ in equilibrium with the melt.

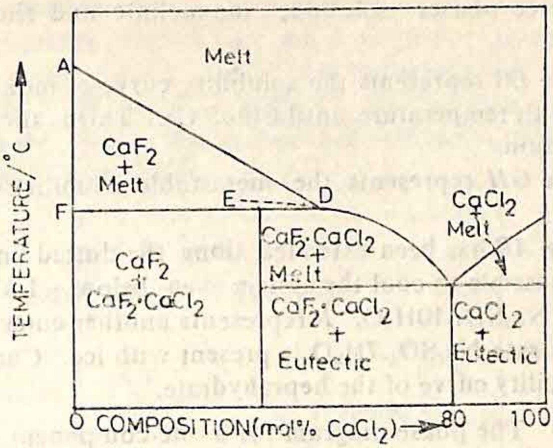


Fig. 12.8 *Phase diagram for CaF_2–$CaCl_2$ system.*

(ii) At *D*, the peritectic reaction between the melt of composition *D* and solid CaF_2 takes place to form a compound $CaF_2.CaCl_2$ as,

$$CaF_2(s) + \text{melt}\,(D) = CaF_2.CaCl_2$$

(ii) The dashed line (in real significance) indicates how the diagram might have looked if the compound had a congruent melting point. The peritectic temperature is 737° in this case.

Sodium Sulphate–Water System

Na_2SO_4 forms two hydrates ($Na_2SO_4.10H_2O$ and $Na_2SO_4.7H_2O$) and exists in two enantiotropic forms (rhombic and monoclinic). The phase diagram is shown in Fig. 12.9.

(i) Curve *AB* represents the freezing point curve of water (ice ⇌ solution).

(ii) Curve *BC* is the solubility curve of $Na_2SO_4.10H_2O$.

(iii) At *C*, $Na_2SO_4.10H_2O$ decomposes into anhydrous Na_2SO_4 and water. This is called the transition temperature (32.383°C).

$$Na_2SO_4.10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$$

(iv) Along *CD*, all three phases coexist, only the amounts differ with composition.

(v) Curve *CE* represents the solubility curve of rhombic Na_2SO_4.

(vi) *E* is the transition point at which rhombic Na_2SO_4 changes into monoclinic Na_2SO_4.

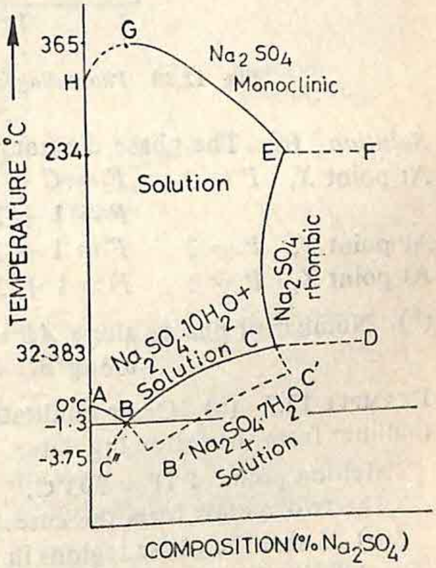


Fig. 12.9 *Phase diagram of Na_2SO_4–H_2O system.*

Along *EF*, three phases—solution, monoclinic and rhombic Na_2SO_4, coexist.

(vii) Curve *EG* represents the solubility curve of monoclinic Na_2SO_4. It decreases with temperature until G(365°C). This is the critical temperature of solution.

(viii) Curve *GH* represents the metastable solubility curve of monoclinic Na_2SO_4.

(ix) Curve *AB* has been extended along the dotted line *BB′*, indicating that it is possible to cool the system even below −1.3°C without the separation of $Na_2SO_4 \cdot 10H_2O$. *B* represents another eutectic point where the second hydrate $Na_2SO_4 \cdot 7H_2O$ is present with ice. Curve *B′C′* represents the solubility curve of the heptahydrate.

Example 12.6 The phase diagram for a one-component system is given in Fig. 12.10.

(a) Calculate the degrees of freedom at points *X*, *Y*, *Z*.

(b) How many phases exist along the lines *AB* and *BC*?

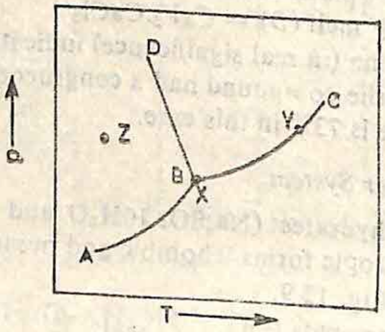


Fig. 12.10 *Phase diagram for one-component system.*

Solution (a) The phase diagram is of one component, $C = 1$

At point *X*, $P = 3$ $\quad F = C + 2 - P$ or

$F = 1 + 2 - 3 = 0$ (invariant)

At point *Y*, $P = 2$ $\quad F = 1 + 2 - 2 = 1$ (univariant)

At point *Z*, $P = 1$ $\quad F = 1 + 2 - 1 = 2$ (bivariant)

(b) Number of phases along $AB = 2$

along $BC = 2$

Example 12.7 (a) Draw qualitatively the phase diagram for gold and thallium from the following data:

Melting point of Tl = 303°C, Melting point of Au = 1065°C

The two metals form the eutectic at 131°C.

(b) Label the phase regions in the diagram.

(c) What will be the composition of the eutectic mixture?

(d) Draw the cooling curves for melts containing 40% Tl and 80% Tl, indicating the separation of metals.

Solution By plotting the graph of temperature (y-axis) against composition of the mixture (x-axis), we get Fig. 12.11. Here, point A corresponds to the melting point of gold and B corresponds to that of pure thallium. C gives the eutectic (131°C). The various areas are also labelled. From the graph, the composition of the eutectic mixture has been found to be 73% thallium.

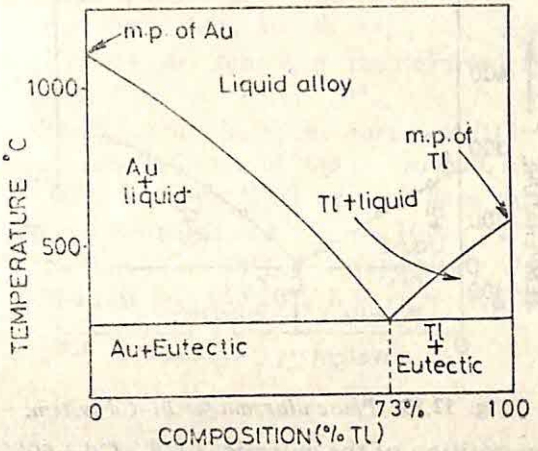
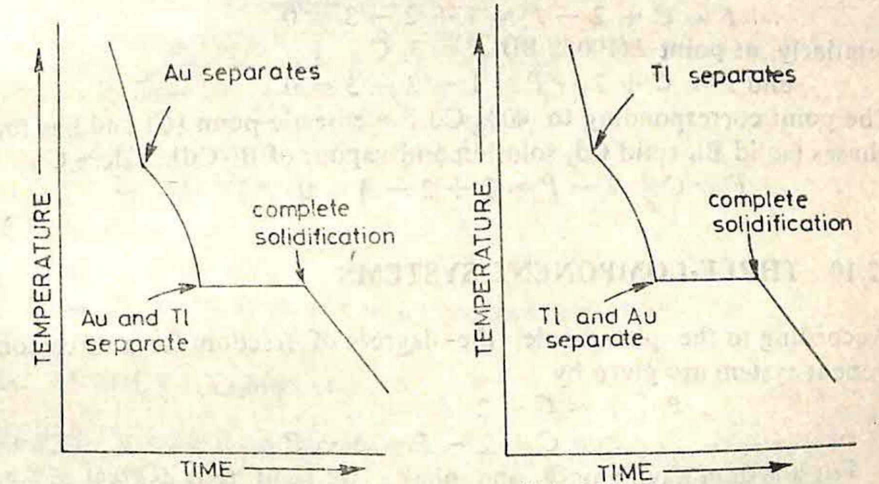


Fig. 12.11 *Phase diagram of Au–Tl system.*



(a) 40% Tl (b) 80% Tl

Fig. 12.12 *Cooling curves for Au–Tl system.*

EXAMPLE 12.8 During the thermal analysis of bismuth-cadmium system, the following initial and final solidification temperatures t_i and t_f, respectively, were observed:

%Cd	0	10	20	30	40	50	60	70	80	90	100
T_i	270	230	205	170	144	193	225	257	280	300	320
T_f	—	144	144	144	144	144	144	144	—	144	—

(a) Construct the phase diagram and label it.
(b) What is the composition of the eutectic?
(c) What will be the degree of freedom at the points corresponding to pure metals and a mixture containing 40% Cd.

Solution (a) The phase diagram for Bi–Cd is shown in Fig. 12.13.

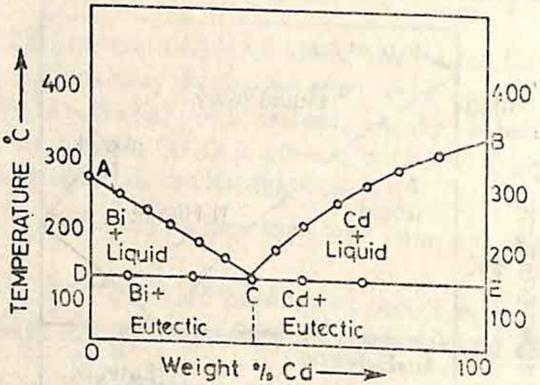


Fig. 12.13 *Phase diagram for Bi–Cd system.*

(b) The composition of the eutectic is 40% Cd+60% Bi.
(c) At the point corresponding to 100% Cd (point *B*), there are three phases (solid, liquid and vapour) and $C = 1$.

$$F = C + 2 - P = 1 + 2 - 3 = 0$$

Similarly, at point B(100% Bi), $P = 3$, $C = 1$

$$\text{and } F = C + 2 - P = 1 + 2 - 3 = 0$$

The point corresponding to 40% Cd is a eutectic point (C) and has four phases (solid Bi, solid Cd, solution and vapour of Bi–Cd). Here $C = 2$

$$F = C + 2 - P = 2 + 2 - 4 = 0$$

12.10 THREE-COMPONENT SYSTEMS

According to the phase rule, the degrees of freedom for a three-component system are given by

$$P + F = C + 2$$

or

$$F = C + 2 - P = 5 - P$$

For a system having only one phase, we need four degrees of freedom, namely, temperature, pressure and the composition of two of the three components. Now, if temperature and pressure are fixed, the number of degrees of freedom becomes two for a single-phase system. For a system consisting of two phases in equilibrium, we need only one degree of freedom at fixed temperature and pressure. On the other hand, for a system consisting of three phases, the degree of freedom is zero. Thus, the maximum number of phases which can occur simultaneously in a three-component system is three at a fixed temperature and pressure.

The most commonly used method to represent three-component systems is the triangular plot which was suggested by Stokes and Roozeboom. In this method, each apex of the triangle is taken as 100% (wt or mole) of the component. For example, the apices *A*, *B* and *C* (Fig. 12.14) represent 100% of *A*, *B* and *C*, respectively. The sides of the triangle are divided into 10 (or sometimes 100) equal parts and the lines parallel to the three sides are drawn. For example, the lines parallel to *BC* dividing *AC* represent the definite composition of *A*, such as *C* gives 0%, *a* gives 10%, . . ., *f* gives 60%, *i* gives 90%, and *A* gives 100%. Similarly, the lines parallel to *AC* dividing *AB* give various compositions of $B(a' = 10\%\ B, b' = 20\%\ B, c' = 30\%\ B, \ldots, f' = 60\%\ B, i = 90\%\ B)$, and the lines parallel to *BA* dividing *BC* give the compositions of $C(a'' = 10\%\ C, b'' = 20\%\ C, d'' = 30\%\ C, \ldots, f'' = 60\%\ C, i'' = 90\%\ C)$, respectively. For example, 20% *A* is expressed by the line *bh'*, and 30% *B* is expressed by the line *c' g''*.

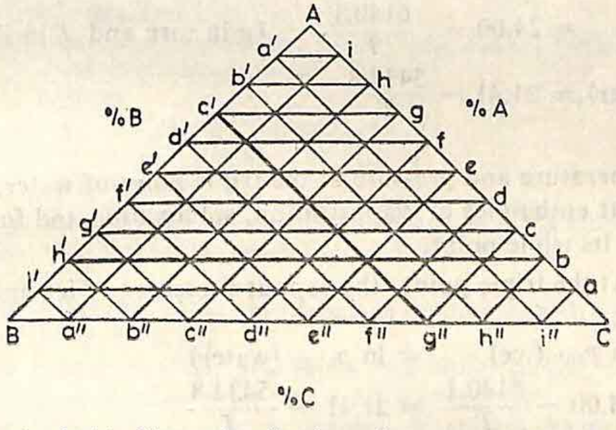


Fig. 12.14 *Triangular plot for a three-component system.*

MISCELLANEOUS EXAMPLES

EXAMPLE 12.9 A lady weighing 50 kg is standing on ice wearing shoes with a sole area of 60 cm² per shoe. What is the melting point of ice under her feet?

Solution Pressure on ice under the feet of the lady,

$$p = \frac{\text{Force}}{\text{Area}} = \frac{mg}{2 \times \text{area of each foot}}$$

$$m = 50\ \text{kg} = 50 \times 10^3 \text{g},\ g = 980.67\ \text{cm s}^{-2}$$

Area of each foot = 60 cm²

$$p = \frac{50 \times 10^3\ \text{g} \times 980.67\ \text{cm s}^{-2}}{2 \times 60\ \text{cm}^2}$$

$$= 4.086 \times 10^5\ \text{g cm}^{-1}\ \text{s}^{-2}$$

$$= 4.086 \times 10^5 \text{ dyn cm}^{-2} \quad [\, 1 \text{ dyn} = 1 \text{ g cm s}^{-2} \,]$$

$$= \frac{4.086 \times 10^5}{1.0133 \times 10^6} \text{ atm} \quad [\, 1 \text{ atm} = 1.0133 \times 10^6 \text{ dyn cm}^{-2}]$$

$$= 0.403 \text{ atm}$$

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fus},\, m}}{T_f\, \Delta V_{\text{fus}}}$$

$$\Delta H_{m,\, \text{fus}} = 6.01 \text{ kJ mol}^{-1},\ \Delta V_{\text{fus}} = V_{m,\, \text{liq}} - V_{m,\, \text{solid}}$$
$$= (0.0180 - 0.0196)\ l \text{ mol}^{-1}$$

$$\frac{dp}{dT} = \frac{(6.01 \times 10^3 \text{ J mol}^{-1}) \times (9.87 \times 10^{-3}\ l \text{ atm J}^{-1})}{(273.15\text{K})(0.0180 - 0.0196)\ l \text{ mol}^{-1}}$$
$$= -135.7 \text{ atm K}^{-1} \quad [\, 1 \text{ J} = 9.87 \times 10^{-3}\ l \text{ atm} \,]$$

Now, $dp = 0.403$ atm

$$dT = -\frac{0.403}{135.7} = -0.003$$

Melting point at 0.403 atm = −0.003°C.

EXAMPLE 12.10 The vapour pressures of ice and water are given by the equations:

$$\ln p_{\text{sub}} \text{ (ice)} = 24.00 - \frac{6140.1}{T} \qquad (p \text{ in torr and } T \text{ in K})$$

$$\ln p_{\text{evap}} \text{ (water)} = 21.41 - \frac{5432.8}{T}$$

Calculate

(a) the temperature and pressure at the triple point of water.

(b) the molar enthalpies of vaporization, sublimation and fusion of water at its triple point.

Solution (a) At the triple point, the vapour pressures of ice and water will be the same.

Therefore, $\ln p_{\text{sub}} \text{ (ice)} = \ln p_{\text{evap}} \text{ (water)}$

or $$24.00 - \frac{6140.1}{T} = 21.41 - \frac{5432.8}{T}$$

or $$24.00 - 21.41 = \frac{6140.1}{T} - \frac{5432.8}{T}$$

or $$T = \frac{707.3}{2.59} = 273.089 \text{ K}$$

The vapour pressure at the triple point can be obtained by substituting this temperature in either of the above equations,

$$\ln p = 24.00 - \frac{6140.1}{273.089} = 1.516$$

or $$p = 4.55 \text{ torr} = 0.006 \text{ atm}$$

(b) We know that

$$\ln p = -\frac{\Delta H_m}{RT} + I$$

Comparing with the given expression for vapour pressure,

$$-\frac{\Delta H_{\text{sub},\, m}}{R} = -6140.1$$

and $$-\frac{\Delta H_{\text{evap},m}}{R} = -5432.8$$

$$\Delta H_{\text{sub},m} = 6140.1 \times 8.314 = 51.05 \text{ kJ mol}^{-1}$$

and $$\Delta H_{\text{evap},m} = 5432.8 \times 8.314 = 45.17 \text{ kJ mol}^{-1}$$

At the triple point,

$$\Delta H_{\text{sub},m} = \Delta H_{\text{fus},m} + \Delta H_{\text{evap},m}$$

or, $$\Delta H_{\text{fus},m} = \Delta H_{\text{sub},m} - \Delta H_{\text{evap},m}$$

$\therefore$ $$\Delta H_{\text{fus},m} = 51.05 - 45.17 = 5.88 \text{ kJ mol}^{-1}$$

QUESTIONS

Numerical Problems

12.1 State how many phases are present in the following systems:
- (a) $I_2 \text{ (s)} \rightleftharpoons I_2 \text{ (g)}$
- (b) $CaCO_3 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$
- (c) $CuSO_4.5H_2O \rightleftharpoons CuSO_4.H_2O\text{(s)} + 4H_2O \text{ (g)}$
- (d) $Fe \text{ (s)} + H_2O \text{ (g)} \rightleftharpoons FeO \text{ (s)} + H_2 \text{ (g)}$
- (e) Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Water vapour
- (f) KCl dissolved in water

12.2 Calculate the number of components present in the following systems:
- (a) A solution of common salt
- (b) NH_3 (g)
- (c) $MgCO_3 \text{ (s)} \rightleftharpoons MgO \text{ (s)} + CO_2 \text{ (g)}$
- (d) $NH_4Cl \text{ (s)} \rightleftharpoons NH_3 \text{ (g)} + HCl \text{ (g)}$
- (e) $H_2O \text{ (s)} \rightleftharpoons H_2O \text{ (l)}$

12.3 How many degrees of freedom will be present in the following systems?
- (a) A gas in equilibrium with its solution in a liquid
- (b) N_2 (g)
- (c) A solution of sodium sulphate in equilibrium with water vapour
- (d) $I_2 \text{ (s)} \rightleftharpoons I_2 \text{ (CCl}_4\text{)}$
- (e) HCl (g) and NH_3 (g) in equilibrium with NH_4Cl (s), when the equilibrium is approached by starting with the solid alone
- (f) Two partially miscible liquids in the absence of vapour

12.4 The melting point of a substance increases by 0.04°C on increasing the pressure by 1 atm. Its molar volumes in the solid and liquid states are 40 ml and 44 ml, respectively. What is its enthalpy of fusion if its melting point is + 23°C.

12.5 (SI Units) Calculate the change in freezing point of ice when the pressure is increased by 10 kPa. The molar volume of water is 18 $\text{cm}^3 \text{ mol}^{-1}$ and that of ice 19.6 $\text{cm}^3 \text{ mol}^{-1}$ (Molar enthalpy of fusion = $6.0 \times 10^3 \text{ J mol}^{-1}$).

12.6 The vapour pressure of a liquid X varies with temperature according to the equation:

$$\log p \text{ (torr)} = 5.910 - \frac{798.2}{T}$$

Calculate the molar enthalpy of vaporization of the liquid.

12.7 The vapour pressure of ice between −10° and 2°C, is given by the equation

$$\log p = 10.42 - \frac{2666.12}{T}$$

and that of liquid water between −10° and 2°C by

$$\log p = 9.30 - \frac{2360.18}{T}$$

What is the triple point of water?

12.8 The atmospheric pressure in a deep valley on a particular day is 1200 torr. Calculate the boiling point of water in that valley on that day (Heat of vaporization = 2.260 kJ g^{-1}).

12.9 The boiling point of a liquid (molar mass = 74, latent heat of vaporisation = 369.8 J g^{-1}) is 33.5°C at 760 torr pressure. At what temperature will it boil when pressure decreases by 10 torr on a particular day?

12.10 The following correlations for the vapour pressure of solid and liquid phosphorus are available

$$\ln p\,(\text{solid}) = -\frac{6621.1}{T} + 12.34$$

$$\ln p\,(\text{liquid}) = -\frac{6310.2}{T} + 11.40$$

where p is in atm and T in K. Calculate

(a) the temperature and pressure of the triple point of phosphorus

(b) the molar enthalpy of fusion of phosphorus at the triple point.

12.11 Calculate the vapour pressure of a liquid at 100°C if it is assumed that it obeys Trouton's rule and its normal boiling point is 110.6°C.

12.12 The following data are given for water at 100°C and 760 torr:
Enthalpy of vaporization = 539.7 J g^{-1}
Molar volume of water = 18.78 cm^3
Molar volume of steam = 30.20 dm^3
Calculate the change in boiling point of water per torr change in atmospheric pressure.

12.13 Figure 12.15 represents the phase diagram for the sulphur system. Find the degrees of freedom at the points *A*, *B*, *C*, *D*, *E*.

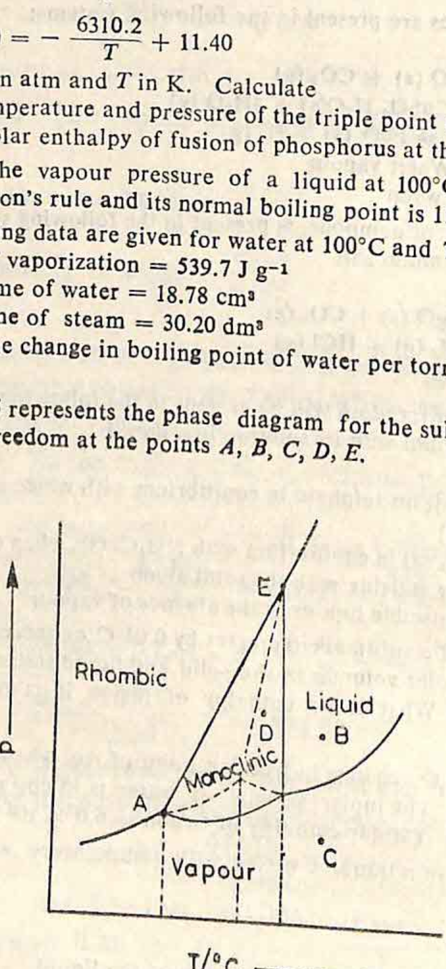


Fig. 12.15

12.14 Figure 12.16 represents the phase diagram for the Cd–Zn system. Calculate the number of phases, components and degrees of freedom at the points *A*, *B*, *C*, *D* and *E*.

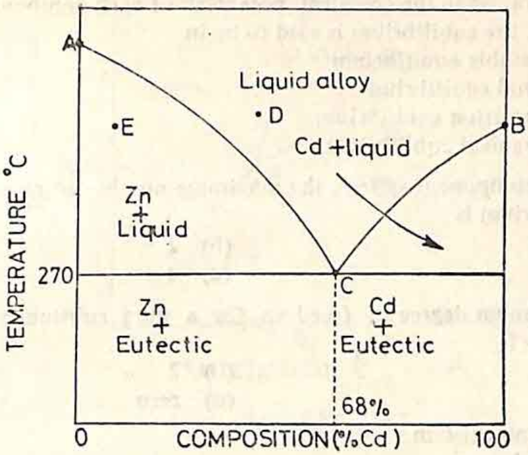


Fig. 12.16

12.15 Construct the phase diagram for the magnesium–zinc system, using the following data:
(a) Melting point of Zn = 419°C
(b) Melting point of Mg = 650°C
(c) Forms two eutectics at 350°C (20 mol % Zn) and at 435°C (92 mol % Zn)
(d) A compound Mg Zn_2 with a true melting point of 575°C, is formed.
Also describe the cooling curve when a mixture of 60 mol % Mg is cooled from 6 0°C to 200°C.

QUIZ QUESTIONS

Type A: Multiple Choice

12.16 Starting with pure NH_4Cl, the following equilibrium is established:

$$NH_4Cl\ (g) \rightleftharpoons NH_3\ (g) + HCl\ (g)$$

The number of components in the system is
(a) one
(b) two
(c) three
(d) may be two or three

12.17 The number of phases of a mixture of four gases enclosed in a container is
(a) 4 (b) 4-1
(c) 1 (d) zero

12.18 In terms of number of phases (*P*), components (*C*) and degrees of freedom (*F*), the phase rule is expressed as
(a) $P + C = F + 2$
(b) $F = P + C - 2$
(c) $P + F = C + 2$
(d) $P - F = C + 2$

12.19 The phase rule was deduced by
(a) Gibbs (b) Thomson
(c) Trouton (d) Henry

12.20 In a system, when the chemical potential of each component is the same for all phases, the equilibrium is said to be in
(a) metastable equilibrium
(b) thermal equilibrium
(c) composition equilibrium
(d) mechanical equilibrium

12.21 In a one-component system, the maximum number of phases that can coexist in equilibrium is
(a) 1
(b) 2
(c) 3
(d) 4

12.22 The maximum degree of freedom for a pure substance under equilibrium conditions is
(a) 1
(b) 2
(c) 3
(d) zero

12.23 Sulphur can exist in
(a) one phase
(b) two phases
(c) three phases
(d) four phases

12.24 The number of degree of freedom for the system

$$NH_4Cl(s) \rightleftharpoons NH_4Cl(g) \rightleftharpoons NH_3(g) + HCl(g) \text{ is}$$

(a) 1
(b) 3
(c) zero
(d) 2

12.25 For a single-component system, the maximum degree of freedom is
(a) 1
(b) 2
(c) 3
(d) between 3 and 6

12.26 The point in the pressure–temperature curve of a water system where the equilibria

ice ⇌ water ⇌ vapour

exists is called the
(a) critical point
(b) triple point
(c) transition point
(d) eutectic point

12.27 The number of degrees of freedom and number of components for a system of sodium chloride solution in water containing undissolved salt, in equilibrium with water vapour, are
(a) 2 , 2
(b) 3 , 2
(c) 1 , 1
(d) 1 , 2

12.28 The number of degrees of freedom at the triple point for the water system is
(a) one
(b) two
(c) three
(d) zero

12.29 The phase diagram for CO_2 is shown in Fig. 12.17. Which of the following statements is not correct regarding this system ?
(a) The curves *AB* and *BC* represent equilibria between solid CO_2 and gas, and liquid CO_2 and gas, respectively.
(b) At 5 atm pressure and $-56.6°C$ temperature, the system has zero degrees of freedom.
(c) At all pressures below 5 atm, heating of solid CO_2 will result in sublimation.
(d) The melting point of CO_2 decreases with increase in pressure.

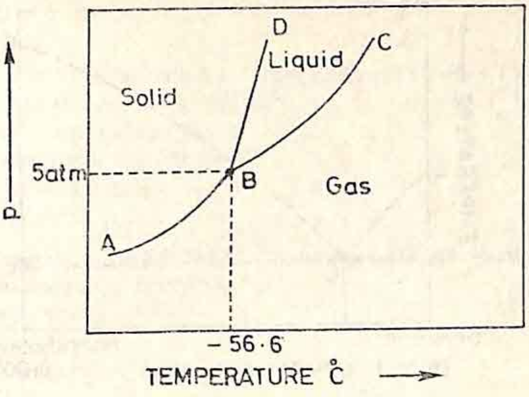


Fig. 12.17

12.30 The point C in the phase diagram of CO_2 (Fig. 12.17) is the
(a) freezing point
(b) triple point
(c) boiling point
(d) critical point

12.31 In the phase diagram of CO_2 (Fig. 12.17), the curve BD represents equilibrium between
(a) solid and gas
(b) solid and liquid
(c) gas and liquid
(d) solid, liquid and gas

12.32 In the phase diagram of CO_2 (Fig. 12.17), the curve BC represents equilibrium between liquid CO_2 and gas. The number of degree of freedom is
(a) zero (b) one
(c) two (d) three

12.33 In the phase diagram of CO_2 (Fig. 12.17), the system is bivariant
(a) at point B
(b) at the critical point
(c) in the region ABD
(d) along BD

12.34 The phase diagram for the benzene–naphthalene system is shown in Fig. 12.18. Which of the following statements is not correct ?
(a) Along curve AC, solid benzene is in equilibrium with liquid solution.
(b) Above curves AC and BC, the two components are present only as a homogeneous liquid solution.
(c) The intensive properties of the system at C are entirely fixed under all conditions of pressure.
(d) At a given pressure, the system is monovariant along BC.

12.35 In the phase diagram of the benzene–naphthalene system (Fig. 12.18), the point C is called the
(a) eutectic point
(b) congruent point
(c) triple point
(d) critical point

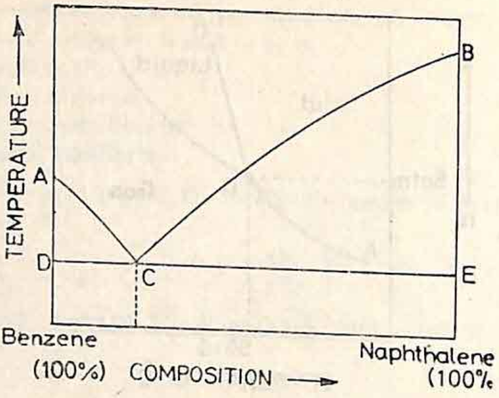


Fig. 12.18

12.36 The region below *CE* corresponds to (Fig. 12.18)

(a) solid benzene+eutectic

(b) solid naphthalene+eutectic

(c) solid benzene+liquid

(d) solid naphthalene+liquid

12.37 The curve *AC* represents equilibrium between (Fig. 12.18)

(a) benzene and naphthalene

(b) benzene and eutectic

(c) benzene and liquid solution

(d) benzene, naphthalene and liquid solution

12.38 The phase diagram for the KI–water system is given in Fig. 12.19. The cryohydric point in the curve is

(a) *A* (b) *B*

(c) *C* (d) *D* and *E*

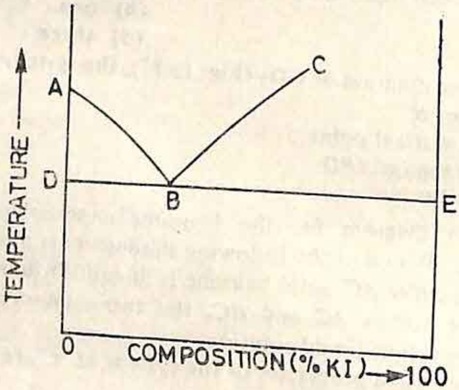


Fig. 12.19

12.39 Which of the following statements is not correct regarding the phase diagram for KI–water system ?

(a) *AB* represents the lowering in freezing point of water on the addition of KI.

(b) Area *CBE* contains two phases—solid KI and solution of KI

(c) The curve *BC* is incomplete and indicates that all the KI becomes soluble in water before its melting point.

(d) At point *B* three phases exist.

12.40 In the phase diagram of the KI–water system, the solubility curve of KI is

(a) AB (b) DB

(c) BC (d) BE

12.41 The temperature at which a compound melts into a liquid of the same composition as the solid is called the

(a) congruent melting point

(b) incongruent melting point

(c) peritectic temperature

(d) metastable point

12.42 The phase diagram for the $FeCl_3$–water system is shown in Fig. 12.20. The diagram shows the formation of

(a) six hydrates

(b) four hydrates

(c) three hydrates

(d) five hydrates

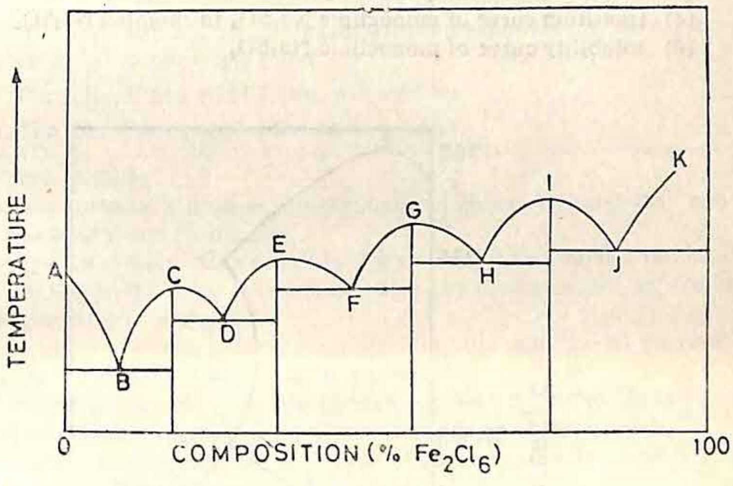


Fig. 12.20

12.43 In the phase diagram of the Fe_2Cl_6–water system (Fig. 12.20), the point G corresponds to the compound

(a) $Fe_2Cl_6 \cdot 12H_2O$

(b) $Fe_2Cl_6 \cdot 7H_2O$

(c) $Fe_2Cl_6 \cdot 6H_2O$

(d) $Fe_2Cl_6 \cdot 5H_2O$

12.44 The number of eutectics in the phase diagram of the Fe_2Cl_6-water system (Fig. 12.20) is

(a) 6 (b) 5

(c) 4 (d) 3

12.45 The region below line LD represents

(a) $Fe_2Cl_6.12H_2O$ + Eutectic ($Fe_2Cl_6.12H_2O + Fe_2Cl_6.7H_2O$)

(b) $Fe_2Cl_6.12H_2O$ + Eutectic (ice + Fe_2Cl_6)

(c) $Fe_2Cl_6.7H_2O$ + Eutectic ($Fe_2Cl_6.12H_2O + Fe_2Cl_6.7H_2O$)

(d) ice + $Fe_2Cl_6.12H_2O$

12.46 In the system CaF_2–$CaCl_2$, (Ref. Fig. 12.8) the reaction

$$CaF_2(s)+\text{Melt} \rightleftharpoons CaF_2.CaCl_2(s)$$

is called

(a) a peritectic reaction
(b) a solubility reaction
(c) formation of compound with congruent melting point
(d) fusion temperature

12.47 A compound with an incongruent melting point decomposes on heating into

(a) a liquid of the same composition as the solid
(b) a new solid phase and a solution with a composition different from that of the solid phase
(c) a new solid phase and a solution with the same composition as that of the solid phase
(d) a solution of fixed composition

12.48 In the phase diagram of Na_2SO_4–water (Fig. 12.21), the curve *EF* represents the

(a) solubility curve of $Na_2SO_4.7H_2O$
(b) metastable solubility curve of monoclinic Na_2SO_4
(c) transition curve of monoclinic Na_2SO_4 to rhombic Na_2SO_4
(d) solubility curve of monoclinic Na_2SO_4

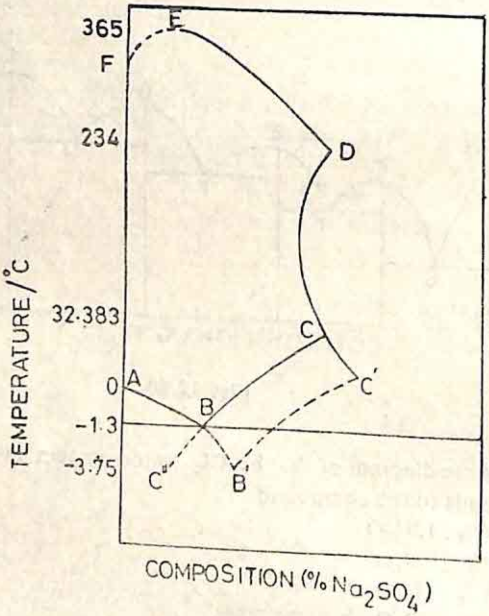


Fig. 12.21

12.49 In the phase diagram of Na_2SO_4–water (Fig. 12.21), the point *D* is the

(a) transition temperature at which rhombic Na_2SO_4 is converted into monoclinic Na_2SO_4
(b) transition temperature at which Glauber's salt changes into monoclinic sodium sulphur
(c) point at which Na_2SO_4-$10H_2O$ changes into $Na_2SO_4.7H_2O$
(d) temperature at which Na_2SO_4 becomes completely soluble in water.

12.50 In the phase diagram of a one-component system (Fig. 12.22), which of the following statements is correct ?

(a) The melting point of the solid increases with increase of pressure

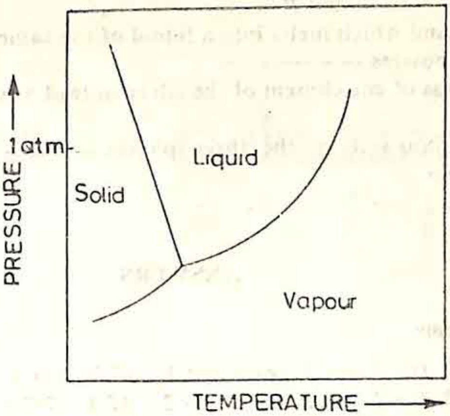


Fig. 12.22

(b) The solid can be in equilibrium with the vapour only at a temperature on or below the triple point

(c) The solid, if heated at 1 atm, will sublime

(d) The three lines meet at the critical point.

Type B: True or False

12.51 In a one-component system, the maximum number of phases that can coexist in true equilibrium is three.

12.52 Super-cooled water is an example of a system in metastable equilibrium.

12.53 According to the phase diagram of water, the melting point of ice decreases with increase in pressure.

12.54 In a system with two phases in equilibrium, the number of degrees of freedom for a one-component system is zero.

12.55 In the phase diagram of sulphur, there are three true triple points.

12.56 The incongruent melting point is also called the peritectic point.

12.57 The degrees of freedom for a solution of sodium sulphate in equilibrium with Glauber's salt are three.

12.58 Metastable equilibrium is possible only in the case of a water system.

12.59 A compound with a congruent melting point melts into a liquid of the same composition as the solid.

12.60 For a system of two miscible components, the eutectic point exists only at a definite temperature.

Type C: Fill in the Blanks

12.61 Cooling of liquids below their freezing point is called ————.

12.62 The property of a chemical compound capable of existing in two or more than two forms is called ————,

12.63 The temperature at which a compound changes into a different compound and a solution with a different composition is called ———— melting point.

12.64 The dissociation of ammonium chloride

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$$

constitutes ———— phases and the number of components is ————.

12.65 The minimum number of independent variables required to completely characterise the composition of each phase in a system is called ————.

12.66 The allotropic forms of solid substances are considered ———— phases.

12.67 The system: ice, water and vapour in equilibrium has $F =$ ————, $C =$ ———— and $P =$ ————.

12.68 A compound which melts into a liquid of the same composition as the solid is said to possess ————.

12.69 The process of enrichment of the silver in lead silver is known as ———— process.

12.70 In the sulphur system, the three phases ———— co-exist in metastable equilibrium.

ANSWERS

Numerical Problems

12.1 (a) 2 (b) 3 (c) 3 (d) 3 (e) 3 (f) 1 ***12.2*** (a) 2 (b) 1 (c) 2 (d) 1 (e) 1
12.3 (a) 2 (b) 2 (c) 2 (d) 2 (e) 1 (f) 2 *12.4* 717.3 cal mol^{-1} *12.5* 0.73 K
12.6 15.28 KJ *12.7* 273.16 K, 0.006 atm *12.8* 386.45 K *12.9* 33.1 *12.10* 330.7
K, 0.00046 atm, 2.6 kJ *12.11* 0.83 atm *12.12* 0.037 *12.13* 0, 2, 2, 2, 0
12.14 $A = 3, 1, 0$; $B = 3, 1, 0$; $C = 4, 2, 0$; $D = 2, 2, 2$; $E = 2, 2, 2$

Quiz Questions

12.16 (a) *12.17* (c) *12.18* (c) *12.19* (a) *12.20* (c) *12.21* (c) *12.22* (b)
12.23 (d) *12.24* (a) *12.25* (b) *12.26* (b) *12.27* (d) *12.28* (d) *12.29* (d)
12.30 (d) *12.31* (b) *12.32* (b) *12.33* (c) *12.34* (c) *12.35* (a) *12.36* (b)
12.37 (c) *12.38* (b) *12.39* (c) *12.40* (c) *12.41* (a) *12.42* (b) *12.43* (d)
12.44 (b) *12.45* (a) *12.46* (a) *12.47* (b) *12.48* (b) *12.49* (c) *12.50* (b)
12.51 True *12.52* True *12.53* True *12.54* False *12.55* True *12.56* True
12.57 False *12.58* False *12.59* True *12.60* False *12.61* Supercooling
12.62 enantiotropy *12.63* incongruent *12.64* two, one *12.65* degree of free-
dom *12.66* different *12.67* 0, 1, 3 *12.68* Congruent melting point *12.69* Pat-
tinson's *12.70* $S_R \, S_L - S_V$

13

Electrical Conductance and Ionic Transport

Electrical conductance in matter is due to the flow of charged particles under an electric field. If these charged particles are electrons, the conductivity is called electronic or metallic. When the current is carried by ions (anions and cations), the conductance is called ionic or electrolytic.

13.1 MEASUREMENT OF THE CONDUCTANCE OF SOLUTIONS

Metallic conductors obey Ohm's law,

$$I = \frac{E}{R} \tag{13.1}$$

where I is the current flowing in amperes, E is the electric potential difference (electromotive force) in volts, and R is the resistance in ohms. Current, in SI Units, is measured in amperes, symbol A, and the resistance in ohms, symbolised Ω.

The resistance of any conductor is proportional to the length (l) and inversely proportional to the area of cross section (a), so that

$$R \propto \frac{l}{a} \quad \text{or} \quad R = \rho \frac{l}{a} \tag{13.2}$$

where the proportionality constant ρ is called *specific resistance* or *resistivity* and depends upon the nature of the material. The reciprocal of resistance is called conductance (C), and the reciprocal of specific resistance is called *specific conductance* or *conductivity* (expressed by κ, kappa).

$$C = \frac{1}{R} \qquad \text{units of } C \text{ are } \Omega^{-1}$$

$$\kappa = \frac{1}{\rho} \qquad \text{units of } \kappa \text{ are } \Omega^{-1}\,\text{cm}^{-1} \text{ or } \Omega^{-1}\,\text{m}^{-1}$$

The SI Units for conductance is siemens, S ($= \Omega^{-1}$).

An unknown resistance is commonly measured by Wheatstone bridge method. For electrolytic solutions, passage of direct current causes electrolysis. This leads to the change of concentration of the electrolyte in solution, besides polarizing the electrodes. To overcome this problem, a modified form of Wheatstone bridge with alternating current (1000–3000 Hz) is used. The conductance is measured in a conductivity cell. It consists of two electrodes, made of platinum foils, kept at a fixed distance. Several types of conductivity cells have been designed.

Conductance depends upon the area of each electrode (a) and the distance between them (l),

$$R = \rho \frac{l}{a}$$

or $$\rho = R\frac{a}{l}$$

or $$\kappa = \frac{1}{\rho} = C\frac{l}{a}$$

The quantity l/a, is called the cell constant and is expressed in cm^{-1} or m^{-1}. The value of the cell constant is determined accurately by measuring the conductance of a standard solution (KCl) of known conductivity.

13.2 EQUIVALENT AND MOLAR CONDUCTANCE

Equivalent conductance, Λ is defined as

$$\Lambda = \frac{1000\,\kappa}{C} \qquad \mathrm{S\ cm^2\ eq^{-1}}$$

where C is the concentration of the solution in equivalent per litre. The units of equivalent conductance are $\Omega^{-1}\ cm^2\ eq^{-1}$ (SI Units: $S\ cm^2\ eq^{-1}$).

A quantity related to the equivalent conductance is molar conductance (Λ_m) defined as

$$\Lambda_m = \frac{1000\,\kappa}{C} \qquad \mathrm{S\ cm^2\ mol^{-1}}$$

where c is in moles per litre and Λ_m has the units $\Omega^{-1}\ cm^2\ mol^{-1}$ (SI Units: $S\ mol^{-1}\ cm^2$).

Note 1. Equivalent conductance expresses the conductance of a volume of solution containing one equivalent of an electrolyte, when placed between two parallel electrodes 1 cm apart, i.e.

$$\Lambda = \kappa \times (\text{vol. of one cm}^3 \text{ containing 1 eq of electrolyte})$$

If C is the concentration of a solution in g eq l^{-1}, then 1 g eq will be present in $1000/C$ ml of the solution. To get the answer in $cm^2\ \Omega^{-1}\ eq^{-1}$, C should be expressed in g eq l^{-1} (for equivalent conductance) or mole l^{-1} (for molar conductance), for numerical problems.

$$\Lambda = \frac{(1000\ \mathrm{cm^3}\ l^{-1})\ (\kappa\ \Omega^{-1}\ \mathrm{cm^{-1}})}{(C\ \mathrm{eq}\ l^{-1})} = \Omega^{-1}\ \mathrm{cm^2\ eq^{-1}}$$

Note 2. Due to use of mole concept these days, the use of term equivalent conductance is discouraged. Thus, instead of saying equivalent conductance of $BaCl_2$, we say molar conductance of $\frac{1}{2}(BaCl_2)$

It should be noted that, on dilution, the number of ions per unit volume decreases. Thus, we should expect a decrease in specific conductance and increase in equivalent or molar conductance because the total number of ions in solution increases due to ionization on dilution. There seems to be a limiting value in very dilute solutions of an electrolyte, called the equivalent conductance at infinite dilution or zero concentration ($\wedge_0$).

It has been noticed that the variation of $\wedge$ with concentration depends to a large extent on the type of electrolyte. In case of strong electrolytes, the change in $\wedge$ with concentration is small, between 4 and 10% only. This is due to interionic attractions which are important at higher concentrations. For weak electrolytes, the change in $\wedge$ with concentration is much larger, so much so that one cannot obtain $\wedge^\circ$ for these electrolytes by extrapolation. The major difference between the types of electrolytes is their extent of dissociation into ions. Strong electrolytes are completely* dissociated at all concentrations whereas, in weak electrolytes, there is equilibrium between dissociated ions and undissociated molecules. However, an electrolyte may behave as a weak electrolyte in one solvent and as a strong electrolyte in another, e.g. HCl is a strong electrolyte in water, but a weak electrolyte in benzene, etc.

EXAMPLE 13.1 A metallic wire of 1 m length and 0.1 mm diameter has a resistance of 10 Ω. Determine its conductance, resistivity and conductivity.

Solution Conductance, $C = \frac{1}{R}$

$$R = 10\ \Omega$$

$$\therefore \quad C = \frac{1}{10} = 0.1\ \Omega^{-1}$$

Resistivity, $\rho = R\frac{a}{l}$

$$l = 1\text{ m} = 100\text{ cm};\ a = \pi r^2,\ r = \frac{0.01}{2}\text{ cm}$$

$$\therefore \quad a = \frac{22}{7} \times \left(\frac{0.01}{2}\right)^2 = 0.7857 \times 10^{-4}\text{ cm}^2$$

$$\rho = \frac{(10\ \Omega) \times (0.7857 \times 10^{-4}\text{ cm}^2)}{(100\text{ cm})}$$

$$= 7.857 \times 10^{-6}\ \Omega\text{ cm}$$

Conductivity, $\kappa = \frac{1}{\rho}$

$$= \frac{1}{7.857 \times 10^{-6}\ \Omega\text{ cm}} = 1.27 \times 10^{5}\ \Omega^{-1}\text{ cm}^{-1}$$

---

*Ion pair formation does take place but is almost negligible.

EXAMPLE 13.2 The resistance of a 0.1 mol dm^{-3} solution of an electrolyte is 60 Ω at 300 K. The dimensions of each electrode in the cell are 0.85 cm × 1.4 cm and the distance between the two electrodes is 1 cm. Calculate (a) cell constant and (b) resistivity (c) conductivity and (d) molar conductance of the solution.

Solution (a) Cell constant $= \dfrac{l}{a}$

$l = 1$ cm, $a = 1.4 \times 0.85 = 1.19$ cm^2

Cell constant $= \dfrac{1}{1.19} = 0.84$ cm^{-1}

(b) Resistivity, $\rho = R\,\dfrac{a}{l}$

$$= \frac{60\ \Omega \times 1.19\ \text{cm}^2}{1\ \text{cm}} = 71.4\ \Omega\ \text{cm}$$

(c) Conductivity, $\kappa = \dfrac{1}{\rho}$

$$= \frac{1}{71.4\ \Omega\ \text{cm}} = 1.4 \times 10^{-2}\ \Omega\ \text{cm}^{-1}$$

(d) Molar conductance, $\Lambda_m = \dfrac{1000\ \kappa}{C}$

$C = 0.1$ mol dm^{-3}

$$\Lambda_m = \frac{1000 \times 1.4 \times 10^{-2}\ \Omega\ \text{cm}^{-1}}{0.1\ \text{mol dm}^{-3}} = 140\ \Omega\ \text{cm}^2\ \text{mol}^{-1}$$

Note In the expression of Λ_m, concentration C should be used in mol dm^{-3}.

EXAMPLE 13.3 (SI Units) The resistance of a cell containing 0.1 mol dm^{-3} KCl solution was found to be 85 Ω. When the same cell was filled with an aqueous 0.052 mol dm^{-3} solution of an electrolyte, the resistance was 96 Ω. Calculate the molar conductance of the electrolyte at this concentration. The specific conductance of 0.1 mol dm^{-3} KCl solution is 1.29×10^{-2} S cm^{-1}.

Solution For calculations of molar conductance,

Cell constant $= R\,\kappa$

$R = 85\ \Omega$, $\kappa = 1.29 \times 10^{-2}$ S cm^{-1}

Cell constant $= 85\ \Omega \times 1.29 \times 10^{-2}$ S cm^{-1} $= 1.1$ cm^{-1}

Specific conductance of the electrolyte solution,

$$\kappa = \frac{\text{Cell constant}}{R}$$

Cell constant $= 1.1$ cm^{-1}, $R = 96\ \Omega$

$$\therefore\ \kappa = \frac{1.1\ \text{cm}^{-1}}{96\ \Omega} = 1.145 \times 10^{-2}\ \text{S cm}^{-1}$$

Molar conductance of the electrolyte solution,

$$\Lambda_m = \frac{1000\ \kappa}{C}$$

$C = 0.052$ mol dm^{-3}

$$\therefore\quad {}_m = \frac{1000 \times (1.145 \times 10^{-2}\ \text{S cm}^{-1})}{(0.052\ \text{mol dm}^{-3})}$$

$$= 220.2\ \text{S cm}^2\ \text{mol}^{-1}$$

EXAMPLE 13.4 The resistance of a 0.2 N solution of an electrolyte in a conductivity cell is 100 ohm at 25°C. What are its conductivity and equivalent conductance if the cell constant is 2.06 cm^{-1}.

Solution Conductivity, $\kappa = \dfrac{\text{Cell constant}}{R}$

Cell constant $= 2.06\ \text{cm}^{-1}$, $R = 100\ \Omega$

$$\therefore \quad \kappa = \frac{2.06\ \text{cm}^{-1}}{100\ \Omega} = 2.06 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$$

Equivalent conductance,

$$\Lambda = \frac{1000\ \kappa}{C}$$

$C = 0.2\ \text{eq}\ l^{-1}$

$$= \frac{1000 \times (2.06 \times 10^{-2}\ \Omega^{-1}\ \text{cm}^{-1})}{0.2\ \text{eq}\ l^{-1}}$$

$$= 103\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

13.3 KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

According to Kohlrausch, the equivalent conductance at infinite dilution for a given salt is equal to the sum of the contributions of the cations and the anions, i.e.

$$\Lambda^\circ_{(AB)} = \lambda^\circ_{(A^+)} + \lambda^\circ_{(B^-)}$$

where $\lambda^\circ_{(A^+)}$ and $\lambda^\circ_{(B^-)}$ are called the limiting equivalent ionic conductances. In other words, this law means that the equivalent ionic conductance for an ion in a given solvent always has the same value, in whichever salt solutions it may be present.

13.4 LIMITING EQUIVALENT CONDUCTANCE OF WEAK ELECTROLYTES

As mentioned earlier, it is not possible to determine accurately the Λ° value, for a weak electrolyte, by extrapolation. However, this can be estimated easily using Kohlrausch's law. For example, for acetic acid,

$$\Lambda^\circ_{(CH_3COOH)} = \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{(H^+)}$$

$$= \lambda^\circ_{(CH_3COO^-)} + \lambda^\circ_{(Na^+)} + \lambda^\circ_{(H^+)} + \lambda^\circ_{(Cl^-)} - \lambda^\circ_{(Na^+)} - \lambda^\circ_{(Cl^-)}$$

$$= \Lambda^\circ_{(CH_3COONa)} + \Lambda^\circ_{(HCl)} - \Lambda^\circ_{(NaCl)}$$

Example 13.5 (SI Units) The molar conductance at infinite dilution for CH_3COONa, HCl and NaCl are 91, 426.2 and 126.5 Ω^{-1} cm^2 mol^{-1}, respectively. Calculate the molar conductance of acetic acid at infinite dilution.

Solution The molar conductance of acetic acid at infinite dilution,

$$\Lambda^{\circ}_{(CH_3COOH)} = \Lambda^{\circ}_{(CH_3COON_2)} + \Lambda^{\circ}_{(HCl)} - \Lambda^{\circ}_{(NaCl)}$$

$$\Lambda^{\circ}_{(CH_3COONa)} = 91.0\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1},\ \Lambda^{\circ}_{(HCl)} = 426.2\ \Omega^{-1}\ \text{cm}^2\text{mol}^{-1},$$

$$\Lambda^{\circ}_{(NaCl)} = 126.5\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

$$\therefore\ \Lambda^{\circ}_{(CH_3COOH)} = 91.0 + 426.2 - 126.5 = 390.7\ \Omega^{-1}\ \text{cm}^2\ \text{mol}^{-1}$$

Example 13.6 The limiting equivalent conductances of sodium chloride, potassium chloride and potassium bromide are 126.45, 149.86 and 151.92 Ω^{-1} cm^2 eq^{-1}, respectively. The limiting equivalent ionic conductance for Br^- is 76.34 Ω^{-1} cm^2 eq^{-1}. What are the limiting equivalent ionic conductances for Na^+ ions ?

Solution

$$\Lambda^{\circ}_{(KBr)} = \lambda^{\circ}_{(K^+)} + \lambda^{\circ}_{(Br^-)}$$

$$\Lambda^{\circ}_{(KBr)} = 151.92\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1},\ \lambda^{\circ}_{(Br^-)} = 76.34\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

$$\therefore\ \lambda^{\circ}_{(K^+)} = \Lambda^{\circ}_{(KBr)} - \lambda^{\circ}_{(Br^-)} = 151.92 - 76.34$$

$$= 85.58\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

$$\Lambda^{\circ}_{(KCl)} = \lambda^{\circ}_{(K^+)} + \lambda^{\circ}_{(Cl^-)}$$

$$\Lambda^{\circ}_{(KCl)} = 149.86\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1},\ \lambda^{\circ}_{(K^+)} = 85.58\ \Omega^{-1}\ \text{cm}^2\text{eq}^{-1}$$

$$\therefore\ \lambda^{\circ}_{(Cl^-)} = \Lambda^{\circ}_{(KCl)} - \lambda^{\circ}_{(K^+)} = 149.86 - 85.58$$

$$= 64.28\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

$$\Lambda^{\circ}_{(NaCl)} = \lambda^{\circ}_{(Na^+)} + \lambda^{\circ}_{(Cl^-)}$$

$$\Lambda^{\circ}_{(NaCl)} = 126.45\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1},\ \lambda^{\circ}_{(Cl^-)} = 64.28\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

$$\therefore\ \lambda^{\circ}_{(Na^+)} = \Lambda^{\circ}_{(NaCl)} - \lambda^{\circ}_{(Cl^-)} = 126.45 - 64.28$$

$$= 58.17\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

13.5 TRANSPORT NUMBER

The fraction of the total current carried by an ion is called its transport number.

$$\text{Transport number of cation } (t_+) = \frac{\text{Current carried by the cation}}{\text{Total current}}$$

$$\text{Transport number of anion } (t_-) = \frac{\text{Current carried by the anion}}{\text{Total current}}$$

If there is only one cation and one anion, then

$$t_+ + t_- = 1$$

or $$t_+ = 1 - t_-$$

or $$t_- = 1 - t_+$$

13.6 DETERMINATION OF TRANSPORT NUMBER

The transport number can be determined by the following methods:

(a) Hittorf's method

(b) Moving boundary method

Hittorf's Method

This method is based on the observation that different concentration changes occur in the vicinity of the electrodes due to different velocities of the ions of an electrolyte. The transference number of a cation is

$$t_+ = \frac{\text{Fall of concentration around anode}}{\text{Total fall in concentration around both the electrodes}}$$

For experimental measurements, a transference cell consists of three compartments, viz. anode, middle and cathode. Electrolysis is carried out using electrodes of some suitable metal. The number of faradays of current flowing through the cell is determined using silver or other coulometers in series with the cell. After passing current for a sufficient length of time, the compartments are analysed to obtain changes in concentration.

Let us assume that the transport number of the Ag^+ ion is to be determined using silver nitrate solution and platinum electrodes. In this procedure, let N_i and N_f be the initial and final number, of equivalents of Ag^+ ion present in a given weight of solvent in the anode compartment. Suppose the weight of copper deposited in the copper coulometer is w g so that $w/31.8 = N_c$ gram equivalents. Then,

$$\text{Fall of concentration around anode} = N_i - N_f$$

$$\text{Transport number of } Ag^+ \ (t_+) = \frac{N_i - N_f}{N_c}$$

In the above example, it has been assumed that the electrodes are passive. This is not always true. For example, if silver electrodes are used, the nitrate ions discharged will attack the silver anode, resulting in an increase in concentration of Ag^+ in the anode compartment. In the above example, the gram equivalents of copper deposited is N_c. Therefore, the increase in concentration of Ag^+ ions in the anode compartment should have been N_c. But the actual increase is $N_f - N_i$. Thus, $N_c - (N_f - N_i)$ represents the fall in concentration due to the movement of Ag^+ ions from the anode compartment. Thus,

$$\text{Transport number of } Ag^+ \text{ ion} = \frac{N_c - (N_f - N_i)}{N_c}$$

Moving Boundary Method

This is based on the principle that when a solution of an electrolyte is placed above a solution of another electrolyte, and a direct current is passed from the bottom to the top, the boundary between the two solutions moves up. This is due to the migration of ions in an electric field. In addition to the solution whose transport number is to be determined (principal electrolyte), another solution is added (indicator electrolyte) to form a boundary between the two. The concentration of the principle electrolyte solution is so adjusted that it is higher than the indicator electrolyte solution. Then, if l is the length through which the boundary moves, A the cross-sectional area of the tube, C the concentration in gram equivalent per litre of solution, and Q faradays current is passed, then

$$\text{Transport number} = \frac{lAC}{1000\,Q}$$

EXAMPLE 13.7 A solution of HCl was electrolysed in a transference cell, between two platinum electrodes. The cathode compartment contained 0.354 g of chloride ions before electrolysis and 0.326 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.

Solution

$$\text{Equivalents of silver deposited} = \frac{0.532}{108} = 4.926 \times 10^{-3} \text{ eq}$$

$$\text{Loss of } Cl^- \text{ ions in cathode compartment} = 0.354 - 0.326 = 0.028 \text{ g}$$

$$\text{Equivalents of } Cl^- \text{ ions lost from cathode compartment} = \frac{0.028}{35.5} = 7.89 \times 10^{-4} \text{ eq}$$

$$t_{(Cl^-)} = \frac{\text{Equivalents of } Cl^- \text{ ions lost from cathode compartment}}{\text{Equivalents of silver deposited in coulometer}}$$

$$= \frac{7.89 \times 10^{-4}}{4.926 \times 10^{-3}} = 0.160$$

and $t_{(H^+)} = 1 - t_{(Cl^-)} = 1 - 0.16 = 0.84°$

EXAMPLE 13.8 The silver nitrate solution from the central compartment of a transference cell weighed 36.58 g and was titrated with 32.7 ml of NH_4CNS solution, 1 ml of which was equivalent to 0.0085 g of $AgNO_3$. The solution from the cathode compartment, weighing 43.17 g, required 29.4 ml of NH_4CNS solution. In the coulometer, in series, the amount of copper deposited was 0.029 g. Calculate the transport number of Ag^+ and NO_3^- ions.

Solution After electrolysis,

43.17 g of cathode solution contains $AgNO_3$

$$= 29.4 \times 0.0085 \text{ g}$$
$$= 0.2499 \text{ g}$$

Amount of water in 43.17 g of solution $= 43.17 - 0.2499$

$$= 42.9201 \text{ g}$$

Before electrolysis

36.5 g of solution contained $AgNO_3 = 32.7 \times 0.0085$

$$= 0.278 \text{ g}$$

Amount of water in 36.5 g of solution $= 36.5 - 0.278$ g

$$= 36.222 \text{ g}$$

Now, 42.9201 g of water before electrolysis will have $AgNO_3$

$$= \frac{0.278}{36.222} \times 42.9201$$
$$= 0.3294 \text{ g}$$

Loss at cathode $= 0.3294 - 0.2499 = 0.0795$ g $AgNO_3$

$$= \frac{0.0795}{170} \text{ g eq of } AgNO_3 = 4.676 \times 10^{-4}$$

Number of equivalents of copper deposited in coulometer $= \dfrac{0.029}{31.8}$

$$= 9.12 \times 10^{-4} \text{ eq}$$

$$t_{(NO_3^-)} = \frac{\text{Loss at cathode in equivalents}}{\text{Equivalents of copper deposited in coulometer}}$$
$$= \frac{4.676 \times 10^{-4}}{9.12 \times 10^{-4}}$$
$$= 0.513$$

and $t_{(Ag^+)} = 1 - 0.513 = 0.487$

EXAMPLE 13.9 In the Hittorf cell using silver electrodes and $AgNO_3$ as an electrolyte, a certain amount of current was passed which deposited 9.886×10^{-4} g equivalent of silver in the coulometer. The anode compartment had the composition 28.235 g H_2O and 0.099 g of $AgNO_3$ before electrolysis and 28.435 g of water and 0.1874 g of $AgNO_3$ after electrolysis. Calculate the transport number of the NO_3^- ion.

Solution At the anode, after electrolysis,

28.435 g of water has $AgNO_3 = 0.1874$ g

At the anode, before electrolysis,

28.235 g of water has $AgNO_3 = 0.099$ g

$$28.435 \text{ g of water has } AgNO_3 = \frac{0.099 \times 28.435}{28.235} = 0.1 \text{ g}$$

Increase in concentration after electrolysis $= 0.1874 - 0.1$

$= 0.0874$ g $AgNO_3$

or $= \dfrac{0.0874}{170} = 5.141 \times 10^{-4}$ g eq $AgNO_3$

Amount of electricity passed $= 9.886 \times 10^{-4}$ g eq. As a result of passing current, there should be an increase in the anode compartment of $Ag^+ = 9.886 \times 10^{-4}$ g eq. This means that $(9.886 - 5.141) \times 10^{-4} = 4.745 \times 10^{-4}$ g eq of Ag^+ ions must have migrated from the anode.

$$t_{(Ag^+)} = \frac{\text{Equivalent loss at anode}}{\text{Equivalent of current passed}} = \frac{4.745 \times 10^{-4}}{9.886 \times 10^{-4}}$$
$$= 0.480$$

$$\therefore \quad t_{(NO_3^-)} = 1 - 0.480 = 0.520$$

Example 13.10 In a moving-boundary method, a current of 25 mA was passed for 80 s. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 16.8 cm towards the cathode. Calculate the transport numbers of H^+ and Cl^- ions. (The cross-sectional area of the glass tube is 1.00×10^{-5} m^2).

Solution Transport number of H^+,

$$t_{(H^+)} = \frac{lAC}{1000\ Q}$$

$l = 16.8$ cm $= 16.8 \times 10^{-2}$ m, $A = 1.0 \times 10^{-5}$ m^2, $C = 0\ 01$ mol dm^{-3}

$Q = 25.0 \times 10^{-3}$ A $\times 80$ s/96500 F

$$t_{(H^+)} = \frac{(16.8 \times 10^{-2}\ \text{m}) \times (1.0 \times 10^{-5}\ \text{m}^2) \times (0.01\ \text{mol dm}^{-3})}{1000 \times \dfrac{25.0 \times 10^{-3} \times 80}{96500}}$$
$$= 0.81$$

$$t_{(Cl^-)} = 1 - t_{(H^+)} = 1 - 0.81 = 0.19$$

13.7 LIMITING IONIC EQUIVALENT CONDUCTANCES

With the knowledge of the transport number of the ion and limiting equivalent conductances of the electrolyte, the limiting ionic equivalent conductances can be determined from the relation,

$$\lambda^\circ_+ = \Lambda^\circ\, t^\circ_+ \quad \text{and} \quad \Lambda^\circ_- = \Lambda^\circ\, t^\circ_-$$

where $\lambda^\circ_\pm$ are the limiting ionic equivalent conductances of cations and anions, respectively.

13.8 ABSOLUTE VELOCITY OR IONIC MOBILITY

The actual velocity of an ion depends upon the potential gradient. If the potential gradient is 1 V cm^{-1}, the velocity of the ion is called its absolute velocity or ionic mobility. It may be defined as the distance travelled by an ion per second under a potential gradient of 1 volt per cm. It can be shown that

$$\text{Ionic mobility } (u_\pm) = \frac{\text{Equivalent ionic conductance}}{\text{Faraday in coulombs}}$$

Example 13.11 The ionic conductances of Li^+, Na^+ and K^+ are 38.6, 50.1 and 73.5 $\Omega^{-1}\, cm^2\, eq^{-1}$, respectively. Calculate their ionic mobilities.

Solution Ionic mobility of an ion:

$$u_\pm = \frac{\lambda^\circ_\pm}{F}$$

$$u_{(Li^+)} = \frac{38.6\ \Omega^{-1}\ cm^2\ eq^{-1}}{96500\ C\ eq^{-1}} = 4.0 \times 10^{-4}\ \Omega^{-1}\ cm^2\ C^{-1}$$

$$= 4 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

$$[\, C = A\,s = C\,\Omega = A\,s\,\Omega,\ A\,\Omega = V\ \therefore C^{-1}\,\Omega^{-1} = V^{-1}\,s^{-1}]$$

$$u_{(Na^+)} = \frac{50.1\ \Omega^{-1}\ cm^2\ eq^{-1}}{96500\ C\ eq^{-1}} = 5.2 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

$$u_{(K^+)} = \frac{73.5\ \Omega^{-1}\ cm^2\ eq^{-1}}{96500\ C\ eq^{-1}} = 7.6 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

Example 13.12 The limiting equivalent conductance of silver nitrate is 133.36 $\Omega^{-1}\, cm^2\, eq^{-1}$. Transport number of the silver ion is 0.475.

(a) What are the limiting equivalent ionic conductances of silver and nitrate ions ?

(b) What are their ionic mobilities ?

Solution (a) Limiting ionic equivalent conductance,

$$\lambda^\circ_\pm = \Lambda^\circ\, t^\circ_\pm$$

$$\Lambda^\circ_{(AgNO_3)} = 133.36\ \Omega^{-1}\ cm^2\ eq^{-1},\ t^\circ_+ = 0.475$$

$$\lambda_{(Ag^+)} = 133.36 \times 0.475 = 63.35\ \Omega^{-1}\ cm^2\ eq^{-1}$$

$$\lambda^\circ_{(NO_3^-)} = \Lambda^\circ_{(AgNO_3)} - \lambda^\circ_{(Ag^+)} = 133.36 - 63.35$$

$$= 70.01\ \Omega^{-1}\ cm^2\ eq^{-1}$$

(b) Ionic mobility $= \dfrac{\lambda^\circ_\pm}{F}$

$$\text{Ionic mobility of } Ag^+ = \frac{63.35}{96500} = 6.56 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

$$\text{Ionic mobility of } NO_3^- = \frac{70.01}{96500} = 7.25 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

EXAMPLE 13.13 The ionic equivalent conductances of Na^+ and Cl^- ions in 0.1 molar sodium chloride are 45 and 63 Ω^{-1} cm^2 mol^{-1}. What are their ionic mobilities and transport numbers ?

Solution

$$\text{Ionic mobility of } Na^+ = \frac{\lambda_{(Na^+)}}{F} = \frac{45}{96500} = 4.66\times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

$$\text{Ionic mobility of } Cl^- = \frac{\lambda_{(Cl^-)}}{F} = \frac{63}{96500} = 6.53 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$$

Transport number,

$$t_{(Na^+)} = \frac{\lambda_{(Na^+)}}{\lambda_{(Na^+)} + \lambda_{(Cl^-)}} = \frac{45}{45+63} = 0.417$$

$$t_{(Cl^-)} = 1 - t_{(Na^+)} = 1 - 0.417 = 0.583$$

13.9 IMPORTANT APPLICATIONS OF CONDUCTANCE MEASUREMENTS

The important applications of conductance measurements are:

Determination of Degree of Dissociation of Weak Electrolytes

The degree of dissociation (α) is calculated from the equivalent conductance Λ_c of the solution at concentration C and Λ° as

$$\alpha = \frac{\Lambda_c}{\Lambda^\circ}$$

Λ° is obtained from Kohlrausch's law. For a weak acid or base dissociating into two ions, the dissociation constant is given by

$$K = \frac{C\alpha^2}{1-\alpha} = \frac{C\Lambda_c}{\Lambda^\circ(\Lambda^\circ - \Lambda_c)}$$

Solubility of Sparingly Soluble Salts

If a pure sample of a sparingly soluble salt is shaken with conductivity water, it forms a saturated solution. The conductivity of the solution is measured and the equivalent conductance calculated from the λ° of the ions. This is then related to the concentration to calculate solubility:

$$\Lambda^\circ = \frac{\kappa \times 1000}{C} \quad \text{or} \quad C = \frac{\kappa \times 1000}{\Lambda^\circ}$$

where C gives the solubility in gram equivalent/litre.

Conductometric Titration

During a titration, the concentration of ions changes when the titrant is added to the titre. This change in concentration is easily detected by the conductometric method. Thus, depending upon the titration, the conductance of a solution may increase, decrease, or remain approximately constant till the end point. After the end point, due to the additional amount of electrolyte added, the conductance may further change (increase or remain constant). The plot between conductance of solution and volume of titrant added is called the *conductometric titration curve.* The end point is detected by the break in the curve. Some important titration curves are given below:

(a) *Titration of a strong acid and strong base* (e g. $HCl + NaOH$)

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$

In the beginning, H^+ ions are replaced by slow-moving Na^+ ions and the conductance decreases (Fig. 13.1). After the end point, Na^+ and OH^- ions increase and hence the conductance increases.

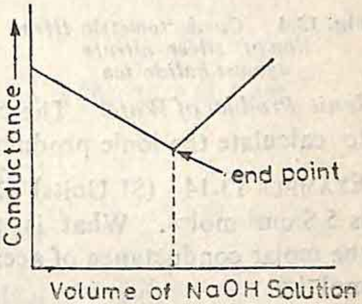


Fig. 13.1 *Conductometric titration of a strong acid (HCl) and a strong base (NaOH).*

(b) *Titration of a weak acid against a strong base* (e.g. $CH_3COOH + NaOH$)

$$CH_3COOH + Na^+ + OH^- \longrightarrow CH_3COO^- + Na^+ + H_2O$$

After an initial decrease due to the titration of free hydrogen ions, the conductance increases because of the net gain of CH_3COO^- and Na^+ ions (as neutralization proceeds) (Fig. 13.2). After neutralization, the conductance increases sharply due to an excess of Na^+ and OH^- ions.

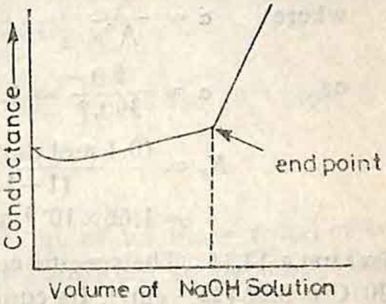


Fig. 13.2 *Conductometric titration of a weak acid (CH_3COOH) and a strong base (NaOH).*

(c) *Titration of a strong acid against a weak base* (e.g. $HCl + NH_4OH$)

$$H^+ + Cl^- + [NH_4OH] \rightarrow NH_4^+ + Cl^- + H_2O$$

The conductance decreases initially because of the replacement of fast-moving H^+ ions by slow-moving NH_4^+ ions (Fig. 13.3). After neutralization, the further addition of weakly ionised NH_4OH does not make much change.

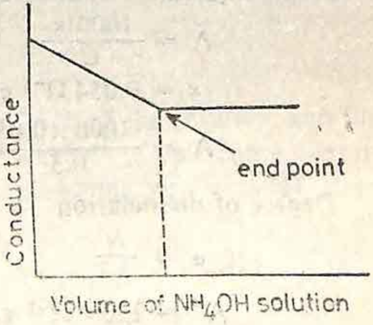


Fig. 13.3 *Conductometric titration of a strong acid (HCl) against a weak base (NH_4OH).*

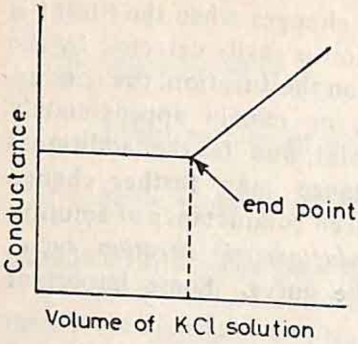


Fig. 13.4 *Conductometric titration of silver nitrate against halide ion*

(d) *Titration of silver nitrate against halide ion* (e.g. $AgNO_3 + KCl$)

$$Ag^+ + NO_3^- + K^+ + Cl^- \rightarrow K^+ + NO_3^- + AgCl$$

Initially, conductance remains almost constant because Ag^+ ions are replaced by K^+ ions and both have almost the same mobility (Fig. 13.4). After the end point, it increases because of the addition of more and more K^+ and Cl^- ions.

Ionic Product of Water The conductometric method has also been used to calculate the ionic product of water.

EXAMPLE 13.14 (SI Units) Molar conductance of 0.1 molar acetic acid is 5 S cm² mol⁻¹. What is the dissociation constant of acetic acid if the molar conductance of acetic acid at infinite dilution is 390.7 S cm² mol⁻¹ ?

Solution Dissociation constant of acetic acid

$$K_a = \frac{C\,\alpha^2}{(1-\alpha)}$$

where $$\alpha = \frac{\Lambda}{\Lambda^\circ}$$

or $$\alpha = \frac{5.0}{390.7} = 1.28\times10^{-2},\ C = 0.1 \text{ mol dm}^{-3}$$

$$K_a = \frac{(0.1 \text{ mol dm}^{-3}) \times (1.28\times10^{-2})^2}{(1-1.28\times10^{-2})}$$
$$= 1.66\times10^{-5} \text{ mol dm}^{-3}$$

EXAMPLE 13.15 The specific conductivity of a 0.5 N solution of KCl at 20°C is 0.054 Ω⁻¹ cm⁻¹. Its equivalent conductance at infinite dilution is 130.4 Ω⁻¹ cm² eq⁻¹. Calculate the apparent degree of dissociation of 0.5 N KCl at 20°C.

Solution Equivalent conductance,

$$\Lambda = \frac{1000\,\kappa}{C}$$

$$\kappa = 0.054\ \Omega^{-1}\text{ cm}^{-1},\ C = 0.5 \text{ eq } l^{-1}$$

$$\Lambda = \frac{1000\times0.054}{0.5} = 108\ \Omega^{-1}\text{ cm}^2\text{ eq}^{-1}$$

Degree of dissociation

$$\alpha = \frac{\Lambda}{\Lambda^\circ}$$

$$\Lambda^\circ = 130.4\ \Omega^{-1}\text{ cm}^2\text{ eq}^{-1}$$

$$\therefore \qquad \alpha = \frac{108}{130.4} = 0.828$$

Note KCl is a strong electrolyte and is completely dissociated. The apparent degree of dissociation is due to interaction, which make it a non-ideal solution.

EXAMPLE 13.16 The conductivity of a saturated solution of $BaSO_4$ is $3.06\times10^{-6}\ \Omega^{-1}\ cm^{-1}$. The equivalent conductance of $BaSO_4$ at infinite dilution is $143\ \Omega^{-1}\ cm^2\ eq^{-1}$. What is the solubility of $BaSO_4$ at 25°C in (a) gram equivalents per litre (b) moles per litre (c) grams per litre? (d) Calculate the solubility product of $BaSO_4$.

Solution Equivalent conductance,

$$\Lambda = \frac{1000\ \kappa}{C}$$

where C gives the solubility (g eq l^{-1}), $\kappa = 3.06\times10^{-6}\ \Omega^{-1}\ cm^{-1}$

$$\Lambda = 146\ \Omega^{-1}\ cm^2\ eq^{-1}$$

(a) $\therefore\ C = \dfrac{1000\ \kappa}{\Lambda} = \dfrac{1000\times3.06\times10^{-6}}{146}$

$$= 20.96\times10^{-6}\ eq\ l^{-1}$$

(b) Solubility $= \dfrac{20.96\times10^{-6}}{2} = 10.48\times10^{-6}\ mol\ l^{-1}$

[Molar mass = 2×Eq. wt.]

(c) Solubility $= 10.48\times10^{-6}\times233 = 2.44\times10^{-3}\ g\ l^{-1}$

[Molar mass of $BaSO_4$ = 233)

(d) Solubility product, $K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right]$

$$\left[Ba^{2+}\right] = 10.48\times10^{-6}\ mol\ l^{-1},\ \left[SO_4^{2-}\right] = 10.48\times10^{-6}\ mol\ l^{-1}$$

$$K_{sp} = (10.48\times10^{-6})\times(10.48\times10^{-6})$$
$$= 1.1\times10^{-10}\ (mol\ l^{-1})^2$$

EXAMPLE 13.17 In the titration of 100 ml of a dilute solution of hydrochloric acid with 0.5 N NH_4OH, the following conductance data are obtained:

Vol. of NH_4OH added (ml)	4	6	8	10	12	14	15	17
Resistance of solution (Ω)	76	68	62	57	53	50	49.5	49

What is the normality of the acid?

Solution The graph between conductance ($1/R$) of the solution and the volume of NH_4OH added (Fig. 13.5) gives a break in the curve corresponding to volume 12.5 ml. Therefore, volume of NH_4OH used = 12.5 ml.

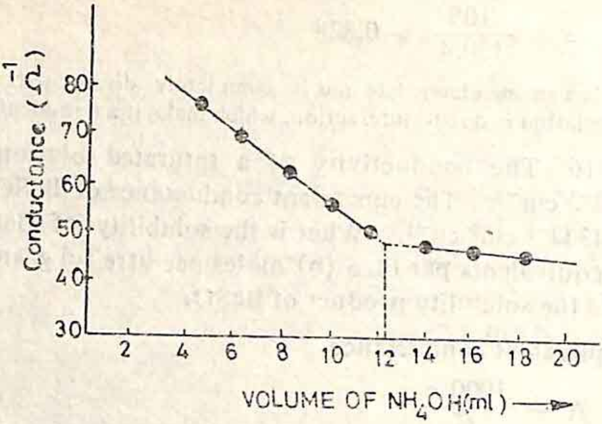


Fig. 13.5 *The graph between conductance of the solution and the volume of NH_4OH added.*

$$\text{Now,}\quad \underbrace{N_1V_1}_{\text{acid}} = \underbrace{N_2V_2}_{\text{alkali}}$$

$$N_1 \times 100 = 0.5 \times 12.5$$

$$\therefore \quad N_1 = \frac{0.5 \times 12.5}{100} = 0.0625 \text{ N}$$

MISCELLANEOUS EXAMPLES

EXAMPLE 13.18 (SI Units) A glass tube of 2 cm internal diameter is fitted with platinum electrodes 50 cm apart. The tube is filled with a 0.1 N solution of KCl at 25°C (specific conductance = 0.0129 S cm^{-1}). What will be the current passing through the solution if a potential difference of 1.234 V is applied across the electrodes ?

Solution Cell constant $= \dfrac{l}{a}$

$$l = 50 \text{ cm},\ a = \pi r^2 = \frac{22}{7} \times \left(\frac{2}{2}\right) = 3.14 \text{ cm}^2$$

$$\therefore \quad \text{cell constant} = \frac{50}{3.14} \text{ cm}^{-1}$$

$$R = \frac{\text{Cell constant}}{\kappa} = \frac{\frac{50}{3.14} \text{ cm}^{-1}}{0.0129 \text{ S cm}^{-1}} = 1234\ \Omega$$

$$\text{Now } I = \frac{E}{R}$$

$$E = 1\ 234 \text{ V},\ R = 1234\ \Omega$$

$$I = \frac{1.234}{1234} = 0.001 \text{ A or 1 mA}$$

EXAMPLE 13.19 (SI Units) What must be the ratio of HCl and KCl in a solution if the transference number of the H^+ ion is 0.53 ? The limiting ionic equivalent conductances are $\lambda_{(H^+)} = 349.8$, $\lambda_{(K^+)} = 73.5$ and $\lambda_{(Cl^-)} = 76.3$ S cm² mol⁻¹.

Solution Let the concentrations of HCl and KCl in a solution, in which the transference number of $H^+ = 0.53$, be C_1 and C_2, respectively.

The transport number of H^+

$$t_{(H^+)} = \frac{C_{(H^+)}\ \lambda_{(H^+)}}{C_{(H^+)}\ \lambda_{(H^+)} + C_{(K^+)}\ \lambda_{(K^+)} + C_{(Cl^-)}\ \lambda_{(Cl^-)}}$$

$$= \frac{C_1\ \lambda_{(H^+)}}{C_1\ \lambda_{(H^+)} + C_2\ \lambda_{(K^+)} + (C_1 + C_2)\ \lambda_{(Cl^-)}}$$

Dividing the numerator and denominator by C_2,

$$t_{(H^+)} = \frac{\frac{C_1}{C_2}\ \lambda_{(H^+)}}{\frac{C_1}{C_2}\ \lambda_{(H^+)} + \lambda_{(K^+)} + \left(1 + \frac{C_1}{C_2}\right) \lambda_{(Cl^-)}}$$

$$\frac{C_1}{C_2}\ \lambda_{(H^+)} = \left[\frac{C_1}{C_2}\ \lambda_{(H^+)} + \lambda_{(K^+)} + \left(1 + \frac{C_1}{C_2}\right) \lambda_{(Cl^-)}\right] t_{(H^+)}$$

or
$$\frac{C_1\ \lambda_{(H^+)}}{C_2\ t_{(H^+)}} = \frac{C_1}{C_2}\ \lambda_{(H^+)} + \lambda_{(K^+)} + \lambda_{(Cl^-)} + \frac{C_1}{C_2}\ \lambda_{(Cl^-)}$$

$$\frac{C_1}{C_2}\left[\lambda_{(H^+)}\left(\frac{1}{t_{(H^+)}} - 1\right) - \lambda_{(Cl^-)}\right] = \lambda_{(K^+)} + \lambda_{(Cl^-)}$$

$$\therefore \quad \frac{C_1}{C_2} = \frac{\lambda_{(K^+)} + \lambda_{(Cl^-)}}{\lambda_{(H^+)}\left(\frac{1}{t_{(H^+)}} - 1\right) - \lambda_{(Cl^-)}} = \frac{73.5 + 76.3}{349.8\left(\frac{1}{0.53} - 1\right) - 76.3}$$

$$= 0.64$$

$$C_{(HCl)} = 0.64\ C_{(KCl)}$$

EXAMPLE 13.20 The specific conductance of an 0.1 N acetic acid solution at 18°C is 0.000471 Ω⁻¹ cm⁻¹ and that of 0.001 N sodium acetate is 0.0000781 Ω⁻¹ cm⁻¹. What is the degree of dissociation of acetic acid at the above dilution and temperature if the ionic conductivity of the H^+ ion is 349.8 and that of Na^+ ion is 44.4 Ω⁻¹ cm² eq⁻¹ (sodium acetate is regarded as completely dissociated)?

Solution Equivalent conductance,

$$\Lambda_{(CH_3COOH)} = \frac{\kappa \times 1000}{C}$$

$$\kappa = 0.000471\ \Omega^{-1}\ \text{cm}^{-1},\ C = 0.1$$

$$\therefore \quad \Lambda_{(CH_3COOH)} = \frac{0.000471 \times 1000}{0.1} = 4.71\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

$$\Lambda_{(CH_3COONa)} = \frac{\kappa \times 1000}{C}$$

$$\kappa = 0.0000781,\ C = 0.001$$

$$\Lambda_{(CH_3COONa)} = \frac{0.0000781 \times 1000}{0.001} = 78.1\ \Omega^{-1}\ \text{cm}^2\ \text{eq}^{-1}$$

Now, $\Lambda_{(CH_3COONa)} = \lambda_{(CH_3COO^-)} + \lambda_{(Na^+)}$

$\lambda_{(Na^+)} = 44.4\ \Omega^{-1}\ cm^2\ eq^{-1}$

$78.1 = \lambda_{(CH_3COO^-)} + 44.4$

or $\lambda_{(CH_3COO^-)} = 78.1 - 44.4 = 33.7\ \Omega^{-1}\ cm^2\ eq^{-1}$

$\Lambda^\circ_{(CH_3COOH)} = \lambda_{(CH_3COO^-)} + \lambda_{(H^+)} = 33.7 + 318.0 = 351.7$

Degree of dissociation, $\alpha = \dfrac{4.71}{351.7} = 0.0134$

QUESTIONS

Numerical Problems

13.1 The conductivity of a 0.1 N potassium chloride solution at 25°C is 0.012886 $\Omega^{-1}\ cm^{-1}$. The resistance of a conductivity cell filled with this solution at 25°C was found to be 100 Ω. What is its cell constant? When filled with another solution, its resistance was 20 Ω. What is the conductivity of the second solution?

13.2 (SI Units) The resistance of a 3×10^{-4} mol dm^{-3} aqueous solution of an electrolyte and a sample of water are $6.5 \times 10^4\ \Omega$ and $7.5 \times 10^6\ \Omega$, respectively at 25°C. The cell constant of the conductance cell is 2.540 cm^{-1}. Calculate the molar conductance of the solution.

13.3 (SI Units) The molar conductivity of a 0.025 mol dm^{-3} aqueous potassium chloride solution is 150 $\Omega^{-1}\ cm^2\ mol^{-1}$. Its resistance in the cell was found to be 80 Ω. What is the cell constant?

13.4 A conductivity cell, when filled with 0.02 M KCl (conductivity = 0.002768 $\Omega^{-1}\ cm^{-1}$) has a resistance of 457.3 Ω. What will be the conductivity and equivalent conductance of a 0.05 N $CaCl_2$ solution if the same cell, filled with this solution, has a resistance of 202 Ω ?

13.5 Determine the resistance of a conducting cell filled with a 0.01 N solution of an electrolyte whose equivalent conductance is 419 $\Omega^{-1}\ cm^2\ eq^{-1}$. The cell constant is 0.88 cm^{-1}.

13.6 The resistance of a cell filled with 5×10^{-5} M $LaCl_3$ solution is 22.5 Ω. Calculate the molar conductance of the solution. The cell consists of two electrodes of equal area ($2.5 \times 10^{-3}\ m^2$) separated by 0.01 m.

13.7 The limiting equivalent conductance of ammonium chloride at infinite dilution is 149.7 $\Omega^{-1}\ cm^2\ eq^{-1}$. Calculate the limiting equivalent conductance of NH_4OH at infinite dilution, given that the ionic mobilities of OH^- and Cl^- are 2.05×10^{-3} and $7.93 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$, respectively.

13.8 (SI Units) The ionic mobility of sodium ion in water at 298 K is 5.29×10^{-4} $cm^2\ s^{-1}\ V^{-1}$. Calculate the equivalent conductance of the sodium ion.

13.9 In 0.1 N HCl at 0°C, the mobilities of H^+ and Cl^- are 36.5×10^{-4} and $7.9 \times 10^{-4}\ cm^2\ s^{-1}\ V^{-1}$, respectively. Calculate
(a) the equivalent conductance of 0.1 N HCl.
(b) the conductivity of 0.1 N HCl.

13.10 (SI Units) Calculate the molar conductance of AgCl at infinite dilution at 298 K. The molar conductance at infinite dilution of $AgNO_3$, NaCl and $NaNO_3$ are 133.3, 126.4 and 121.5 $\Omega^{-1}\ cm^2\ mol^{-1}$, respectively.

13.11 The molar ionic conductances at infinite dilution, at 25°C, for certain ions are given below :

ion	Li^+	NH_4^+	Ba^{2+}	Cl^-	SO_4^{2-}
$\lambda^\circ_\pm$ (Ω^{-1} cm^2 mol^{-1})	38.7	73.4	127.3	76.3	159.6

Estimate the molar conductances of aqueous LiCl, $(NH_4)_2SO_4$ and $BaCl_2$.

13 12 A solution of silver nitrate was electrolyzed between platinum electrodes. The fall in concentration of silver ions in the anode compartment is 1.2 g per unit volume, while the corresponding fall in the cathode compartment is 0.93. Calculate the transport numbers of Ag^+ and NO_3^- ions.

13.13 (SI Units) A decimolar solution of copper sulphate was electrolyzed between platinum electrodes. After passing current, a fall in concentration of 0.00325 g eq occurred in the anode compartment. The weight of copper deposited in a coulometer placed in series was found to be 0.422 g. Calculate the transport number of Cu^{2+} and SO_4^{2-} ions.

13.14 A solution containing 10.6 mg of silver per 10 g of the solution was electrolyzed between silver electrodes. The anode liquid after electrolysis, contained 17,176 mg of silver per 10 g of anode solution. In a silver coulometer in series, 13.47 mg of silver was deposited. Calculate the transport number of silver and nitrate ions.

13.15 An aqueous solution containing 9.6% by wt of $CuSO_4$ was electrolyzed between copper electrodes. After electrolysis, 5.726 g of $CuSO_4$ was present in 54.56 g of the anode solution. The weight of silver deposited in a silver coulometer placed in series was 0.9328 g. Calculate the transport number of Cu^{2+} ions.

13.16 (SI Units) In a moving-boundary experiment in aqueous sodium chloride of 10 mol m^{-3} concentration, the sodium ion moved 8.5 cm towards the cathode on passing 2.1 C of electricity through the solution. The area of cross section of the tube was 1×10^{-5} m^2. Calculate the transport number of Na^+ and Cl^- ions.

13.17 In a moving-boundary method, a current of 20 mA was passed for 15 min. If the radius of the capillary is 4 mm, calculate the distance moved by H^+ in a solution of concentration 50 mol m^{-3} (Transport number of $H^+ = 0.830$).

13.18 In a moving boundary experiment with 1 N KCl solution using cadmium chloride as indicator, a current of 0,0115 A was passed for 30 min and the boundary moved through a volume of 0.106 ml. Calculate the transport number of K^+ ion.

13.19 The equivalent conductance of sodium chloride at infinite dilution is 126.45 Ω^{-1} cm^2 eq^{-1}, and the transport number of the sodium ion under these conditions is 0.401. What is the ionic mobility of the Cl^- ion at this temperature ?

13.20 At 298 K, the resistivity of an aqueous solution of an organic acid (RCOOH) of concentration 8×10^{-3} mol dm^{-3} was 465 Ω cm^{-1}. The limiting molar conductance at infinite dilution for this acid is 478 Ω^{-1} cm^2 mol^{-1}. Calculate α at that concentration.

13 21 The specific conductance of a saturated solution of CaF_2 at 18°C is 4.3×10^{-5} Ω^{-1} cm^{-1}. The equivalent ionic conductances at infinite dilution for Ca^{2+} and F^- ions are 51 and 47 cm^2 Ω^{-1} eq^{-1}, respectively. Assuming that only Ca^{2+} and F^- ions are present in the solution, calculate

(a) the solubility of CaF_2 in g l^{-1}

(b) the solubility product of CaF_2

The specific conductance of the water used for making the solution is 0.05×10^{-5} Ω^{-1} cm^{-1}.

13.22 (SI Units) The equivalent conductance of 0.1 M NH_4Cl solution is 128.75 S cm^2 eq^{-1}. Its equivalent conductance in the presence of excess of NH_4OH is 128.75 S cm^2 eq^{-1}. What is the degree of hydrolysis if $\Lambda^\circ_{(HCl)}$ at this temperature is 426.6 S cm^2 eq^{-1}?

13.23 Calculate the molar conductance at infinite dilution for the salt
COONa
| from the following data:
COOK
$\lambda_{(Na^+)} = 50.1$, $\lambda_{(K^+)} = 73.5$ and $\lambda_{(ox^{2-})} = 74.1$ S cm^2 eq^{-1}.

13.24 The mobilities of Na^+ and Cl^- at 25°C, in water, are 5.19×10^{-4} cm^2 s V^{-1} and 7.91×10^{-4} cm^2 s V^{-1}. What proportion of the current is carried by the chloride ions in a 1×10^{-3} mol dm^{-3} NaCl solution? What will be the change in the fraction of current carried by the chloride ion on adding an equal volume of 1×10^{-3} mol dm^{-3} HCl?

13.25 Sodium chloride, weighing 58.5 g, is dissolved in 10,000 *l* of water at 25°C, giving a solution which may be regarded as infinitely dilute. If the ionic conductances of Na^+ and Cl^- ions are 50.1 and 76.3 Ω^{-1} cm^2 eq^{-1}, respectively, calculate:
(a) the equivalent conductance of the solution
(b) the conductivity of the solution.
(c) the resistance of a cylindrical column of such a solution whose height is 20 cm and base radius 2 cm.

QUIZ QUESTIONS

Type A: Multiple Choice

13.26 Electrolytic conduction is due to the movement of
(a) electrons (b) ions
(c) atoms (d) electrons as well as ions

13.27 Which of the following solutions of NaCl will have the highest specific conductance?
(a) 0.001 N (b) 0.01 N
(c) 0.1 N (d) 1.0 N

13.28 Equivalent conductance can be expressed in terms of specific conductance (κ) and concentration (C) gram equivalent per dm^{-3} as
(a) $\kappa \times C$ (b) $\dfrac{\kappa \times 1000}{C}$
(c) $\dfrac{\kappa \times C}{1000}$ (d) $\kappa \times C \times 1000$

13.29 Which of the following statements is not correct ?
(a) The conductance of one cm^3 of a material is called specific conductance.
(b) Specific conductance increases while equivalent conductance decreases on progressive dilution.
(c) The limiting equivalent conductances of weak electrolytes cannot be determined by extrapolation of the plot of Λ against concentration.
(d) The conductivity of metals is due to the movement of electrons.

13.30 Equivalent conductance is expressed in the units
(a) S cm^{-1} eq^{-1} (b) S cm^2 eq^{-1}
(c) S cm^2 eq^{-1} (d) S cm^2 eq

13.31 The fraction of the total current carried by an ion is called its
(a) ionic mobility (b) transport number
(c) limiting ionic conductance (d) none of these

13.32 Which of the following plots will be obtained for a conductometric titration of a strong acid against a weak base?

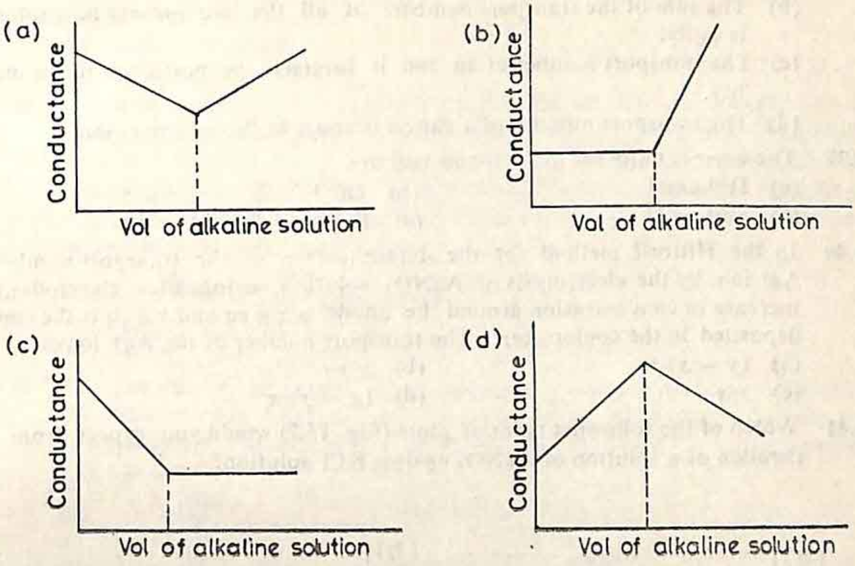


Fig. 13.6

13.33 If for a solution of an electrolyte, t_+ is the transport number of the cation, then the transport number of the anion t_- is equal to

(a) $t_+/2$ (b) $1 - t_+$

(c) $1 + t_+$ (d) $(1 - t)/2$

13.34 If Λ_c is the equivalent conductance at concentration C and Λ° is the limiting equivalent conductance, the the degree of dissociation α is

(a) $\alpha = \Lambda^\circ - \Lambda_c$ (b) $\alpha = 1 - \dfrac{\Lambda_c}{\Lambda^\circ}$

(c) $\alpha = \dfrac{\Lambda_c}{\Lambda^\circ}$ (d) $\alpha = \dfrac{\Lambda^\circ - \Lambda_c}{\Lambda^\circ}$

13.35 Which of the following relations expresses Kohlrausch's law ?

(a) $\alpha = \dfrac{\Lambda}{\Lambda^\circ}$ (b) $t_+^\circ \times \Lambda^\circ = \lambda_+^\circ$

(c) $\lambda_+^\circ = \Lambda^\circ - \lambda_-^\circ$ (d) $\lambda_+^\circ/96500 = \lambda_-^\circ$

13.35 When a concentrated solution of an electrolyte is diluted

(a) its specific conductance increases

(b) its equivalent conductance decreases

(c) its specific conductance decreases and equivalent conductance increases

(d) both specific and equivalent conductance increase

13.37 If in a solution of 1–1 electrolytes, u_+ and u_- are the velocities of cations and anions, respectively, the transport number of cations is equal to

(a) $\dfrac{u_+}{u_+ + u_-}$ (b) $\dfrac{u_-}{u_+ + u_-}$

(c) $\dfrac{u_+ - u_-}{u_+}$ (d) $1 - \dfrac{u_+}{u_+ - u_-}$

13.38 Which of the following statements is correct?

(a) The transport number of a cation is equal to its equivalent conductance divided by the specific conductance.

(b) The sum of the transport numbers of all the ions present in a solution is unity.

(c) The transport number of an ion is inversely proportional to its mobility.

(d) The transport number of a cation is equal to that of the anion.

13.39 The correct units for the cell constant are

(a) $\Omega^{-1}\ \text{cm}^{-1}$ (b) cm^{-1}

(c) cm^2 (d) $\Omega\ \text{cm}^{-1}$

13.40 In the Hittorff method for the determination of the transport number of Ag^+ ion, by the electrolysis of $AgNO_3$ solution, using silver electrodes, the increase in concentration around the anode is x g eq and y g eq is the copper deposited in the coulometer. The transport number of the Ag^+ ion is

(a) $(y - x)/y$ (b) x/y

(c) y/x (d) $(x - y)/x$

13.41 Which of the following types of plots (Fig. 13.7) would you expect from the titration of a solution of $AgNO_3$ against KCl solution?

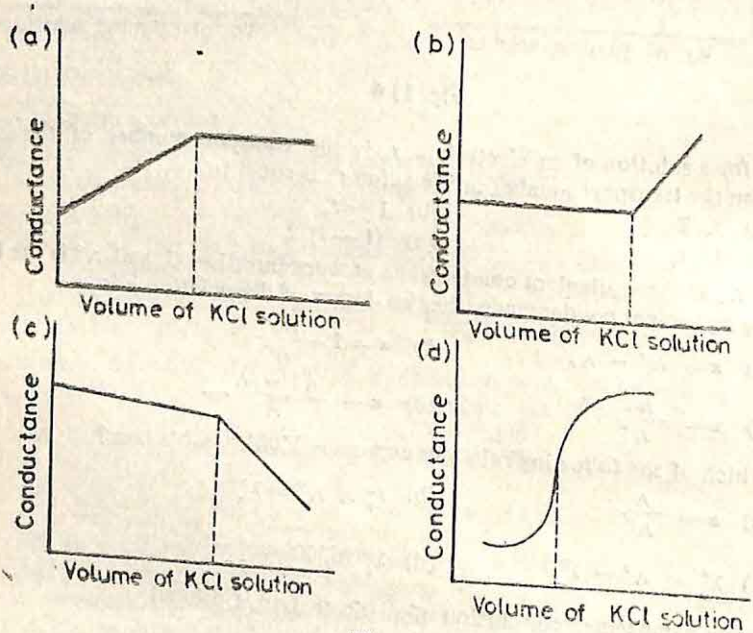


Fig. 13.7

13.42 For a weak electrolyte, the dissociation constant (K) is related to the equivalent conductance at concentration C (Λ_c) and Λ° by

(a) $K = \dfrac{\Lambda_c^2}{\Lambda^\circ(1 - \Lambda_c)}$ (b) $K = \dfrac{C\Lambda_\circ^2}{\Lambda_c(\Lambda_c - \Lambda^\circ)}$

(c) $K = \dfrac{C\Lambda_c^2}{\Lambda^\circ(\Lambda^\circ - \Lambda_c)}$ (d) $K = \dfrac{C\Lambda_c^2}{(\Lambda^\circ - \Lambda_c)^2}$

13.43 During the titration of a weak acid against NaOH, the conductance of the solution after the neutralization point
(a) is constant
(b) decreases
(c) varies irregularly
(d) increases

13.44 In the determination of the transport number of Ag^+ in $AgNO_3$ solution, using platinum electrodes, the concentrations of the anode compartment have been found to be a and b g eq per 100 g of water in the solution after and before electrolysis. The weight of the copper deposited in a copper coulometer placed in the series was found to be c g. The transport number of Ag^+ is (at. wt of Cu = 63.6)
(a) $\frac{a-b}{c} \times 63.6$ (b) $\frac{c-(a+b)}{31.8}$
(c) $\frac{31.8\, a(-b)}{c}$ (d) $\frac{b-a}{c} \times 31.8$

13.45 The specific conductance of a saturated solution of silver chloride is $\kappa\ \Omega^{-1}\ cm^{-1}$. The limiting ionic conductances of Ag^+ and Cl^- ions are x and y, respectively. The solubility of silver chloride, in g l^{-1}, is (molar mass of AgCl = 143.5)
(a) $\frac{\kappa \times 1000}{x-y}$ (b) $\frac{\kappa}{x+y} \times 143.5$
(c) $\frac{\kappa \times 1000 \times 143.5}{x+y}$ (d) $\frac{x+y}{\kappa} \times \frac{1000}{143.5}$

13.46 According to the Debye-Huckel theory of strong electrolytes, an ion moving in an atmosphere of oppositely charged ions experiences a drag. This effect is known as the
(a) asymmetric effect (b) electrophoretic effect
(c) inter-ionic effect (d) concentration effect

13.47 The equivalent conductance of a 1 N solution of an electrolyte is nearly
(a) the same as its specific conductance
(b) 10^3 times more than its specific conductance
(c) 10^{-3} times its specific conductance
(d) 100 times its specific conductance

13.48 The transport number of H^+ ion in a solution C_1 M in HCl and C_2 M in $BaCl_2$ can be written as

(a) $$\frac{\lambda_{(H^+)}}{\lambda_{(H^+)} + \lambda_{(Ba^{2+})} + 2\lambda_{(Cl^-)}}$$

(b) $$\frac{C_1 \lambda_{(H^+)}}{C_1 \lambda_{(H^+)} + 2C_2 \lambda_{(Ba^{2+})} + (C_1 + 2C_2) \lambda_{(Cl^-)}}$$

(c) $$\frac{C_1 \lambda_{(H^+)}}{C_1 \lambda_{(H^+)} + C_2 \lambda_{(Ba^{2+})} + \lambda_{(Cl^-)}}$$

(d) $$\frac{C_1 \lambda_{(H^+)}}{C_1 \lambda_{(H^+)} + 2C_2 \lambda_{(Ba^{2+})} + 2C_2 \lambda_{(Cl^-)}}$$

13.49 The equivalent conductance ($\wedge$) and molar conductance ($\wedge_m$) of $BaSO_4$ are related as
(a) $\wedge = \frac{\wedge_m}{2}$ (b) $\frac{\wedge}{2} = \wedge_m$
(c) $\wedge = \wedge_m$ (d) $\wedge = \frac{\wedge_m}{4}$

13.50 The equivalent conductance ($\wedge$) is related to the ionic mobility of the cation (u_+) and anion (u_-) as

(a) $\wedge = u_+ + u_-$

(b) $\wedge = \frac{u_+}{2} + \frac{u_-}{2}$

(c) $\wedge = \frac{u_+}{F} + \frac{u_-}{F}$

(d) $\wedge = u_+F + u_-F$

Type B : Multiple Choice (Numerical Problems)

13.51 The conductivity of a 0.1 N KCl solution at 25°C is 0.012886 Ω^{-1} cm^{-1}. The resistance of this solution, placed in a conductivity cell, was found to be 100 Ω. The cell constant of the conductivity cell is

(a) 12.886 cm^{-1}

(b) 1.2886 cm^{-1}

(c) 1.2886 × 10^{-4} cm^{-1}

(d) 0.0012886 cm^{-1}

13.52 The resistance of a 0.01 N solution of an electrolyte was found to be 200 Ω at 25°C. The equivalent conductance of the solution is (cell constant = 0.5 cm^{-1})

(a) 25 Ω^{-1} cm^2 eq^{-1}

(b) 40 Ω^{-1} cm^2 eq^{-1}

(c) 250 Ω^{-1} cm^2 eq^{-1}

(d) 125 Ω^{-1} cm^2 eq^{-1}

13.53 The equivalent conductance of a 0.1 N solution of an electrolyte was found to be 400 Ω^{-1} cm^2 eq^{-1}. The cell constant of the cell is 1.0 cm^{-1}. What is the resistance of the solution?

(a) 200 Ω

(b) 2000 Ω

(c) 400 Ω

(d) 25 Ω

13.54 The limiting equivalent conductances of NaCl, KCl and KBr are 126.5, 150.0 and 152.0 S cm^2 eq^{-1}, respectively. The limiting equivalent ionic conductance for Br^- is 76 S cm^2 eq^{-1}. The limiting equivalent ionic conductance for Na^+ ions would be

(a) 128.5

(b) 124.5

(c) 74.0

(d) 52.5

13.55 The limiting ionic conductance of an ion is 48.25 S cm^2 eq^{-1}. Its ionic mobility is

(a) 5.0 × 10^{-4} cm^2 V^{-1} s^{-1}

(b) 5.0 × 10^{-6} cm^2 V^{-1} s^{-4}

(c) 48.25 Ω^{-1} cm^2 eq^{-1}

(d) cannot be calculated

13.56 The specific conductance of a 0.1 N solution of an electrolyte at 20°C is 0.0004510 S cm^{-1}. The equivalent conductance of this electrolyte at infinite dilution is 300 S cm^2 eq^{-1}. The degree of dissociation of the electrolyte is

(a) 0.66

(b) 0.15

(c) 0.015

(d) 0.066

13.57 The equivalent conductance of sodium chloride at infinite dilution, in a solvent, is 110 Ω^{-1} cm^{-2} eq^{-1}. The transport number of the sodium ion under these conditions is 0.40. The limiting equivalent conductance of the Cl^- ion at this temperature would be

(a) 44 Ω^{-1} cm^2 eq^{-1}

(b) 66 Ω^{-1} cm^2 eq^{-1}

(c) $\frac{66}{96500}$ cm^2 V^{-1} s^{-1}

(d) $\frac{44}{66}$ cm^2 eq^{-1}

13.58 The equivalent conductances of CH_3COONa, HCl and NaCl at infinite dilutions are 91, 426 and 126 S cm^2 eq^{-1}, respectively, at 25°C. The equivalent conductance at infinite dilution for CH_3COOH would be

(a) 209 S cm^2 eq^{-1} (b) 391 S cm^2 eq^{-1}
(c) 461 S cm^2 eq^{-1} (d) none of these

13.59 A solution of HCl was electrolyzed in a transference cell between platinum electrodes. The cathode compartment contained 0.354 g of chloride ions before electrolysis and 0.326 g afterwards. A silver coulometer in series had a deposit of silver equivalent to 0.1750 g of Cl^- ion. The transport number of the H^+ ion would be

(a) 6.25 (b) 0.84
(c) 0.16 (d) 0.26

13.60 The ionic conductances of Na^+ and Cl^- ions in 0.1 M sodium chloride are 45 and 65 Ω^{-1} cm^2 eq^{-1}. The transport number of the Cl^- ion would be

(a) 0.409 (b) 0.591
(c) 0.152 (d) $1-0.152$

13.61 The specific conductance of a saturated solution of AgCl at 25°C is 2.07×10^{-6} Ω^{-1} cm^{-1}. The limiting equivalent ionic conductances of Ag^+ and Cl^- ions are 62 and 76 Ω^{-1} cm^2 eq^{-1}, respectively. What is the solubility of AgCl?

(a) 2.0×10^{-5} g eq l^{-1} (b) 1.5×10^{-8} g eq l^{-1}
(c) 1.5×10^{-5} g eq l^{-1} (d) 2.0×10^{-6} g eq l^{-1}

13.62 In the moving-boundary method, the transport number of H^+ ion has been found to be 0.8304 in HCl solution. The transport number of the Cl^- ion would be

(a) 1.8304 (b) 0.2696
(c) 0.1696 (d) cannot be predicted

13.63 The equivalent conductance of ammonium chloride at infinite dilution is 150 Ω^{-1} cm^2 eq^{-1}. The ionic conductances of OH^- and Cl^- ions are 198 and 76 Ω^{-1} cm^2 eq^{-1}. What is the equivalent conductance of ammonium hydroxide at infinite dilution?

(a) 272 Ω^{-1} cm^2 eq^{-1} (b) 124 Ω^{-1} cm^2 eq^{-1}
(c) 274 Ω^{-1} cm^2 eq^{-1} (d) 424 Ω^{-1} cm^2 eq^{-1}

13.64 The molar conductance of sodium acetate is 91 Ω^{-1} cm^2 mol^{-1} of hydrochloric acid is 426 Ω^{-1} cm^2 mol^{-1} and of sodium chloride is 126 Ω^{-1} cm^2 mol^{-1}. The limiting equivalent ionic conductance of the H^+ ion is 341. What is the limiting ionic equivalent conductance of acetate ion?

(a) 391 Ω^{-1} cm^2 eq^{-1} (b) 120 Ω^{-1} cm^2 eq^{-1}
(c) 471 Ω^{-1} cm^2 eq^{-1} (d) 40 Ω^{-1} cm^2 eq^{-1}

13.65 During the electrolysis of a solution of silver nitrate using silver electrodes, an increase in 0.000155 g eq of the silver ion has been observed in the anode compartment. At the same time, 0.0003 g eq of copper was deposited in the copper coulometer placed in series. The transport number of the Ag^+ ion would be

(a) 0.516 (b) 0.483
(c) 0.464 (d) $1-0.483$

Type C: True or False

13.66 In electrolytic conductance, current is carried by electrons.

13.67 At infinite dilution of an electrolyte, the equivalent conductances of cations and anions are independent of each other.

13.68 Electronic conductance decreases while ionic conductance increases with increase in temperature.

13.69 The molar conductance decreases on dilution.

13.70 The limiting equivalent conductance of weak electrolytes can be obtained by extrapolation of the Λ versus concentration plot to zero concentration.

13.71 During the measurement of the transport number in a transference cell, there is no change in concentration in the middle compartment.

13.72 The distance travelled by an ion, per second, under a potential gradient of 1 V cm^{-1} is called the transport number.

13.73 During electrolysis in a transference cell, there is always fall in concentration of the cation in anode compartment.

13.74 Ostwald's dilution law has been found to hold good in the case of weak electrolytes.

13.75 The conductance of 1 cm^3 of a material is called its specific conductance.

Type D: Fill in the Blanks

13.76 The reciprocal of conductivity is called ———————.

13.77 The units of ——————— are $\Omega^{-1}\ cm^2\ mol^{-1}$.

13.78 Equivalent conductance of electrolyte solution ——————— with increase in temperature.

13.79 The units of ionic mobility are ———————.

13.80 In SI units, conductance is expressed in ———————.

13.81 The product of equivalent conductance and viscosity is called ———————.

13.82 On progressive dilution, specific conductance ——————— and equivalent conductance ———————.

13.83 Equivalent ionic conductance/Faraday in coulombs, is called ———————.

13.84 S $cm^2\ eq^{-1}$ are the units for ———————.

13.85 During electrolysis of a solution of silver nitrate using silver electrodes, by Hittorf's method, the concentration of silver ions in the anode compartment will ———————.

ANSWERS

Numerical Problems

13.1 1.289 cm^{-1}, 0.6445 $\Omega^{-1}\ cm^{-1}$ *13.2* 129.1 *13.3* 0.3 cm^{-1} *13.4* 6.27×10^{-8},
125.4 *13.5* 210 Ω *13.6* 356 *13.7* 271 *13.8* 51.05 *13.9* 428.4, 0.0428 *13.10*
138.2 *13.11* 115, 306.4, 279.9 *13.12* 0.563, 0.437 *13.13* $t_{(Cu^{++})} = 0.245$,
$t_{(SO_4^{2-})} = 0.755$ *13.14* $t_{(Ag^+)} = 0.486$, $t_{(NO_3^-)} = 0.514$ *13.15* 0.217 *13.16*
$t_{(Na^+)} = 0.39$ $t_{(Cl^-)} = 0.61$ *13.17* 10.9 *13.18* 0.494 *13.19* $7.85 \times 10^{-4}\ cm^2\ V^{-1}\ s^{-1}$
13.20 56% *13.21* (a) 1.69×10^{-2} (b) 4.1×10^{-11} *13.22* 3.36×10^{-5} *13.23*
271.8 *13.24* decreases by 0.27 *13.25* (a) 126.4 (b) 1.26×10^{-5}.

Quiz Questions

13.26 (b) *13.27* (d) *13.28* (b) *13.29* (b) *13.30* (c) *13.31* (b) *13.32* (c)
13.33 (b) *13.34* (c) *13.35* (c) *13.36* (c) *13.37* (a) *13.38* (b) *13.39* (b)
13.40 (a) *13.41* (b) *13.42* (c) *13.43* (d) *13.44* (c) *13.45* (c) *13.46* (a)
13.47 (b) *13.48* (b) *13.49* (a) *13.50* (d) *13.51* (b) *13.52* (c) *13.53* (d)
13.54 (d) *13.55* (a) *13.56* (c) *13.57* (b) *13.58* (b) *13.59* (b) *13.60* (b)
13.61 (c) *13.62* (c) *13.63* (a) *13.64* (d) *13.65* (b) *13.66* False: Current
carried by cations and anions *13.67* True *13.68* True *13.69* False *13.70* False
13.71 True *13.72* False: It is called ionic mobility *13.73* False: There is fall in
concentration if the electrodes are not attacked, but there is increase in concentra-
tion when the electrodes are attacked *13.74* True *13.75* True *13.76* resistivity
13.77 molar conductance *13.78* increases *13.79* $cm^2\ V^{-1}\ s^{-1}$ *13.80* S *13.81*
Walden product *13.82* decreases, increases *13.83* ionic mobility *13.84* equiva-
lent conductance *13.85* increase.

14

Ionic Equilibrium

Many substances, such as acids, bases and salts, on dissolution in water, split into charged particles (cations and anions). Such substances are called electrolytes and the resulting solutions are called electrolytic solutions. All substances do not dissociate into ions to the same extent, rather there is a state of dynamic equilibrium between ions and unionized particles. The different types of equilibria existing in solutions are considered in this chapter.

14.1 STRONG AND WEAK ELECTROLYTES

Substances which, on dissolution, dissociate completely into ions are called strong electrolytes while those which are not completely dissociated are called weak electrolytes.

Most salts, with a few exceptions (such as $HgCl_2$, $CdBr_2$, etc.), are strong electrolytes. They exist as ions even in the solid state, e.g. NaCl, KCl, etc. On the other hand, a large number of acids and bases are weak electrolytes, with the exception of some mineral acids and alkali and alkaline earth metal hydroxides. In the case of solutions of weak electrolytes, undissociated molecules and ions are in equilibrium.

14.2 ARRHENIUS THEORY OF IONIZATION

Arrhenius proposed that a chemical equilibrium exists between the unionized electrolyte species and the ions formed. Such an equilibrium is characterized by a constant known as the ionization or dissociation constant. For an electrolyte AB,

$$\mathrm{AB} \rightleftharpoons \mathrm{A^+ + B^+}$$

$$K' = \frac{a_{(A^+)}\, a_{(B^-)}}{a_{(AB)}} \tag{14.1}$$

where K' is the *thermodynamic dissociation* or *ionization constant*, and it refers to activities. In dilute solutions, the activities may be replaced by concentrations term so that

$$K = \frac{[A^+][B^-]}{[AB]} \tag{14.2}$$

where K is called the *ionization* or *dissociation constant* and terms within square brackets represent concentrations. If, initially, c moles of AB are dissolved in one litre of solution and α is the degree of ionization, then, at equilibrium, the concentrations of the various species are:

$$[AB] = c(1-\alpha), \qquad [A^+] = c\alpha, \qquad [B^-] = c\alpha$$

and

$$K = \frac{c\alpha^2}{1-\alpha} \tag{14.3}$$

For strong electrolytes, $\alpha = 1$ and K is infinity. It may be noted that, at higher concentrations, it becomes necessary to use activities of the species instead of their concentrations. The thermodynamic ionization constant may be obtained by determining K values at different concentrations and then extrapolating to zero concentration.

14.3 ACID BASE EQUILIBRIA

There are three main definitions of acids and bases.

Arrhenius Theory

According to this theory, acids give H^+ (or H_3O^+) ions in aqueous solution while bases give OH^- ions in aqueous solution.* For example, HCl, HNO_3, CH_3COOH, etc. are acids because they give H^+ ions, while NaOH, $Ca(OH)_2$ etc., are bases because they give OH^- ions in aqueous solutions. The strength of an acid or a base depends upon its capacity to ionize into proton or hydroxyl ions, respectively. Acid–base neutralization reactions involve reactions between H^+ and OH^- ions to give water.

Bronsted-Lowry Concept

According to this concept, an acid is a substance which donates a proton while a base is a substance which accepts a proton. For example, HCl, HNO_3, CH_3COOH, etc., are acids because they can donate protons, while NH_3, H_2O, HSO_4^-, etc., are bases because they can accept protons. The acid-base neutralization reaction involves the transfer of a proton from an acid to a base.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NH_3} \rightleftharpoons NH_4^+ + Cl^-$$

---

*Due to strong interactions between a proton and molecules of water, the proton exists as $H_9O_4^+$ ion in aqueous solutions. However, the species is generally represented by H^+ or H_3O^+ in most books. Similarly, OH^- exists as $H_9O_5^-$ but is always written as OH^-. In this book we shall write the species as H^+ and OH^-.

It may be noted that when an acid loses a proton, the residual part behaves as a base and is called the *conjugate base* of an acid. Similarly, a base accepts a proton to form the *conjugate acid.*

$$\underset{\text{acid}}{HCl} \xrightarrow{-H^+} \underset{\text{conjugate base}}{Cl^-}$$

$$\underset{\text{base}}{NH_3} \xrightarrow{+H^+} \underset{\text{conjugate acid}}{NH_4^+}$$

HCl and Cl^-, NH_3 and NH_4^+ are called *conjugate acid-base pairs.* The neutralization may be expressed as.

$$\text{Acid} + \text{Base} \rightleftharpoons \text{Conjugate base} + \text{Conjugate acid}$$

e.g. $HCl + H_2O \rightleftharpoons Cl^- + H_3O^+$

$HCl + NH_3 \rightleftharpoons Cl^- + NH_4^+$

The direction in which the acid-base reaction tends to occur depends upon the relative strengths of the species involved. Obviously, if the acid is strong, its conjugate base is weak, and *vice versa.*

Lewis Concept

According to the Lewis concept, an acid is a substance which can accept a pair of electrons while a base is a substance which can donate a pair of electrons.

The acid-base reaction involves the donation of a pair of electrons from the base to the acid, forming a dative bond.

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{BF_3} \longrightarrow H_3N \rightarrow BF_3$$

$$\underset{\text{acid}}{Ag^+} + \underset{\text{base}}{2CN^-} \longrightarrow [Ag(CN)_2]^-$$

Thus, BF_3, Ag^+, etc. act as acids and NH_3, CN^-, etc. act as bases according to the Lewis concept.

EXAMPLE 14.1 (a) Classify the following into Lewis acids and bases:

S^{2-}, BF_3, Cl^-, C_2H_5OH, $(CH_3)_3N$, Ag^+

(b) What are the conjugate bases of

HS^-, H_3O^+, $[Al(H_2O)_6]^{3+}$, $H_2PO_4^-$

(c) Identity the conjugate acid-base pairs in the following reactions by marking 1 and 2

$NH_3 + HCl \rightleftharpoons NH_4^+ + Cl^-$

$$HNO_3 + CN^- \rightleftharpoons HCN + NO_3^-$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$$

(d) Which of the following can behave as Bronsted acids as well as Bronsted bases?

$H_2O, H_2SO_4, HCO_3^-, H_3PO_4, H_2PO_4^-$

Solution (a) Lewis acids: BF_3, Ag^+

Lewis bases: Cl^-, S^{2-}, C_2H_5OH, $(CH_3)_3N$

(b) Conjugate bases of

$$HS^- \xrightleftharpoons{-H^+} S^{2-}$$

$$H_3O^+ \xrightleftharpoons{-H^+} H_2O$$

$$[Al(H_2O)_6]^{3+} \xrightleftharpoons{-H^+} [Al(H_2O)_5OH]^{2+}$$

$$[H_2PO_4]^- \xrightleftharpoons{-H^+} [HPO_4]^{2-}$$

(c) Conjugate acid-base pairs:

$$\text{Acid}_1 + \text{Base}_2 \rightleftharpoons \text{Conjugate acid}_2 + \text{Conjugate base}_1$$

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

$$HNO_3 + CN^- \rightleftharpoons HCN + NO_3^-$$

$$H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$$

(d) H_2O, HCO_3^-, HPO_4^{2-} can behave both as acids and bases. These are called *amphoteric substances*.

14.4 DISSOCIATION EQUILIBRIA OF ACIDS AND BASES

Different acids and bases have different degrees of ionization or dissociation. These are determined in terms of ionization or dissociation constants.

Dissociation of an Acid in Water

The dissociation equilibrium of an acid (HA) may be represented as

$$HA \rightleftharpoons H^+ + A^-$$

If c is the number of moles of the acid in one litre of the solution and α is the degree of dissociation, then the dissociation constant K_a for the acid is

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha) \times (c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-a} \qquad (14.4)$$

For weak acids α is small so that $1 - \alpha \approx 1$

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}} \quad \text{and } [\text{H}^+] = \sqrt{K_a c} \tag{14.5}$$

Note The above relations are approximate. Generally, if $Ka < 10^{-5}$ we can neglect α in comparison to 1 and solve for α. However, the exact value can be obtained by rearranging Eq. (14.4) as

$$c\alpha^2 + K_a\alpha - K_a = 0$$

Solving the quadratic equation we get

$$\alpha = \frac{-K_a + \sqrt{K_a^2 - 4\,K_a c}}{2c} \tag{14.6}$$

An alternative method is to use the method of successive approximations. The degree of dissociation of a 0.1 M solution of CH_3COOH can be calculated from its K_a value of 1.8×10^{-5} at 25°C as:

$$K_a = \frac{c\alpha^2}{1 - \alpha} = 1.8 \times 10^{-5}$$

Let us first calculate the value of α by assuming $1 - \alpha \approx 1$. Let this approximate value be α_1, i.e.

$$0.1\,\alpha_1^2 = 1.8 \times 10^{-5}$$

$$\alpha_1 = 1.342 \times 10^{-2}$$

As a second approximation, substitute the value of α_1 in the denominator and solve for α. Let the value be α_2

$$\frac{0.1\,\alpha_2^2}{1 - 0.01342} = 1.8 \times 10^{-5}$$

$$\alpha_2^2 = 1.8 \times 0.9866 \times 10^{-4}$$

$$\alpha_2 = 1.333 \times 10^{-2}$$

This procedure is to be continued till the values of α do not differ significantly, i.e.

$$\frac{0.1\alpha_3^2}{1 - 0.01333} = 1.8 \times 10^{-5}$$

$$\alpha_3^2 = 1.8 \times 0.9867 \times 10^{-4}$$

or $$\alpha_3 = 1.333 \times 10^{-2}$$

Since, the values of α_2 and α_3 are the same, this is the correct value, i.e.

$$\alpha = 1.333 \times 10^{-2}$$

The approximate value is greater by only about 0.67% of the correct value.

Dissociation of a Base in Water

The dissociation equilibrium of a base, BOH may be represented as:

$$BOH \rightleftharpoons B^+ + OH^-$$

The dissociation constant K_b may shown to be

$$K_b = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

so that

$$\alpha = \sqrt{\frac{K_b}{c}} \text{ and } [OH^-] = \sqrt{K_b\, c}$$

Strengths of Acids and Bases

Qualitatively, the strengths of acids and bases can be predicted on the basis of dissociation constants. The acid (or a base) having a higher value of dissociation constant is stronger. But, for quantitative comparison, the concentration of H^+ ions should be determined for both acids in solutions of equal molarity, i.e.

$$\frac{\text{Strength of acid HA(1)}}{\text{Strength of acid HA(2)}} = \frac{\left[-K_a(1) + \sqrt{K_a^2(1) + 4\,K_a(1)\,c}\right]}{\left[-K_a(2) + \sqrt{K_a^2(2) + 4\,K_a(2)\,c}\right]}$$

where $K_a(1)$ and $K_a(2)$ are the dissociation constants.

Similarly, for two bases,

$$\frac{\text{Strength of base BOH(1)}}{\text{Strength of base BOH(2)}} = \frac{\left[-K_b(1) + \sqrt{K_b^2\,(1) + 4K_b(1)\,c}\right.}{\left[-K_b(2) + \sqrt{K_b^2\,(2) + 4K_b(2)\,c}\right.}$$

EXAMPLE 14.2 The dissociation constant of acetic acid at 25°C is 1.8×10^{-5}. What is the concentration of hydrogen ion in 0.1 and 0.01 molar acetic acid solutions?

Solution If α is degree of dissociation of acetic acid, then the concentrations of various species in solution are:

$$\underset{c(1-\alpha)}{CH_3COOH} \overset{H_2O}{\rightleftharpoons} \underset{c\alpha}{H^+} + \underset{c\alpha}{CH_3COO^-}$$

$$K_a = \frac{[H^+]\,[CH_3\,COO^-]}{[CH_3COOH]} = \frac{c\alpha^2}{1-\alpha}$$

Assuming $\alpha \ll 1$,

$$K_a = c\alpha^2$$

or

$$\alpha = \sqrt{\frac{K_a}{c}}$$

For $c = 0.1M,\ K_a = 1.8 \times 10^{-5}$

$$\therefore \qquad \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 1.34 \times 10^{-2}$$

$$[H^+] = c\alpha = 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3} \text{ mol } l^{-1}$$

For $c = 0.01\text{M}$, $K_a = 1.8 \times 10^{-5}$

$$\therefore \qquad \alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.01}} = 4.24 \times 10^{-2}$$

$$[H^+] = c\alpha = 0.01 \times 4.24 \times 10^{-2} = 4.24 \times 10^{-4} \text{ mol } l^{-1}$$

EXAMPLE 14.3 The dissociation constant of a base at 25°C is 1.5×10^{-10}. What is the concentration of hydroxyl ion in 0.015 molar solution of the base? What is its degree of dissociation?

Solution If α is the degree of dissociation of the base, then the concentrations of various species in the solution are:

$$\begin{array}{ccccc} BOH & \rightleftharpoons & B^+ & + & OH^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

so that $\qquad K_b = \sqrt{\dfrac{c\alpha^2}{1-\alpha}} \approx c\alpha^2$

If $\qquad \alpha \leqslant 1$

$$\alpha = \sqrt{\frac{K_b}{c}}$$

$$K_b = 1.5 \times 10^{-10}, \qquad c = 0.015\text{M}$$

$$\text{Degree of ionisation, } \alpha = \sqrt{\frac{1.5 \times 10^{-10}}{0.015}} = 1.0 \times 10^{-4}$$

Now $\qquad [OH^-] = ca = 0.015 \times 1.0 \times 10^{-4} = 1.5 \times 10^{-6}$

Dissociation Constants of Polybasic Acids

Acids capable of giving more than one hydrogen ion (or hydronium ion) per molecule are called *polybasic* or *polyprotic* acids. For example, $H_2C_2O_4$, H_2S, H_2CO_3, etc. are dibasic acids and H_3PO_4, H_3AsO_4, etc. are tribasic acids. These dissociate in stages. For example,

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad K_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]}$$

The dissociation constant K_2 is generally smaller than K_1 in any dibasic acid. For example, for the above carbonic acid at 25°C, $K_1 = 4.5 \times 10^{-7}$ and $K_2 = 4.7 \times 10^{-11}$.

Similarly, for tribasic phosphoric acid,

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- ; \qquad K_1 = 7.5 \times 10^{-3}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}; \qquad K_2 = 6.2 \times 10^{-8}$$

$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}; \qquad K_3 = 4.8 \times 10^{-13}$$

Thus, in polybasic acids, the first dissociation constant is large while succeeding ones have small values. Therefore, in these polybasic acids, it can be assumed that $[H^+]$ in solution is mainly due to the first dissociation step. The concentration of hydrogen ion from successive dissociation is negligibly small. However, calculation of the total $[H^+]$ is possible, though difficult.

EXAMPLE 14.4 (a) Calculate the concentration of H_2S, HS^-, S^{2-} and H^+ in a solution of 0.1M H_2S, given that

$$K_1 = 1.1 \times 10^{-7} \quad \text{and} \quad K_2 = 1.0 \times 10^{-14}$$

(b) What will be the concentration of S^{2-} if the solution is 0.1M in HCl also?

Solution $H_2S \rightleftharpoons HS^- + H^+$

$$K_1 \rightleftharpoons \frac{[H^+][HS^-]}{[H_2S]} = 1.1 \times 10^{-7}$$

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

$$K_2 \rightleftharpoons \frac{[H^+][S^{2-}]}{[HS^-]} = 1.0 \times 10^{-14}$$

Since K_2 is considerably smaller than K_1, the $[H^+]$ obtained from the second dissociation may be considered negligible. Let α be the degree of dissociation of H_2S so that

$$\underset{c(1-\alpha)}{H_2S} \rightleftharpoons \underset{c\alpha}{HS^-} + \underset{c\alpha}{H^+}$$

or $$K_1 \rightleftharpoons \frac{c\alpha^2}{1-\alpha}$$

If $c = 0.1M$ and $1 - \alpha$ is almost equal to 1,

$$0.1\alpha^2 = 1.1 \times 10^{-7}$$

or $$\alpha = 1.05 \times 10^{-4}M$$

$$[H^+] = c\alpha = 0.1 \times 1.05 \times 10^{-4}, = 1.05 \times 10^{-5}M = c' \text{ (say)}$$

$$[HS^-] = [H^+] = 1.05 \times 10^{-5} = c'$$

Now, consider the second dissociation

$$HS^- \rightleftharpoons H^+ + S^{2-}$$

Let β be the degree of dissociation of HS^-.

Then, $$[H^+]_{\text{Total}} = [H^+]_{\text{Dissociation I}} + [H^+]_{\text{Dissociation II}}$$

$$= c' + c'\beta$$

$$[HS^-] = [HS^-]_{\text{Dissociation I}} - [HS^-]_{\text{Dissociation II}}$$

$$= c' - c'\beta$$

and $$[S^{2-}] = c'\beta$$

$$K_2 = \frac{[H^+][S^{2-}]}{[HS^-]} = \frac{(c' + c'\beta)(c'\beta)}{(c' - c'\beta)}$$

or $$\frac{c'[(1+\beta)\,c'\beta]}{c'\,(1-\beta)} = \frac{(1+\beta)\,c'\beta}{1-\beta} = K_2$$

Since the value of β is small compared to 1, so that

$$(1+\beta) \approx 1 \approx (1-\beta)$$

$$\therefore \quad c'\beta = K_2$$

$$\therefore \quad [H^+]_{Total} = 1.05 \times 10^{-5} + 1.0 \times 10^{-14}$$

Now, K_2 is very small in comparison to K_1 and can be neglected compared to $[H^+]_{Dissociation\ I}$.

$$[H^+] = 1.05 \times 10^{-5}$$

and $$[S^{2-}] = c'\beta = 1.0 \times 10^{-14}$$

Thus, concentrations are

$[H_2S] = 0.1M$ (dissociation is very small)

$[HS^-] = 1.05 \times 10^{-5}M$

$[H^+] = 1.05 \times 10^{-5}M$

$[S^{2-}] = 1.0 \times 10^{-14}M$

In the presence of HCl, the ionization of H_2S will further decrease and the concentration of H^+ ion will be almost due to HCl alone

Thus, $[H^+] = 0.1M$, $[H_2S] = 0.1M$

so that $$K_1 = \frac{[H^+]\,[HS^-]}{[H_2S]} = \frac{(0.1)\,[HS^-]}{0.1} = 1.1 \times 10^{-7}$$

$$\therefore \quad [HS^-] = 1.1 \times 10^{-7}M$$

Similarly, for the second dissociation,

$$\frac{[H^+]\,[S^{2-}]}{[HS^-]} = \frac{(0.1)\,[S^{2-}]}{1.1 \times 10^{-7}} = 1.0 \times 10^{-14}$$

or $$[S^{2-}] = 1.1 \times 10^{-20}M$$

EXAMPLE 14.5 The dissociation constants of phosphoric acid are $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, $K_3 = 4.8 \times 10^{-13}$.

Calculate the concentrations of H^+, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-} and H_3PO_4 in a 0.1M solution of phosphoric acid.

Solution The main source of $[H^+]$ is the first dissociation step. Let α be the degree of dissociation of phosphoric acid,

$$\begin{array}{ccccc} H_3PO_4 & \rightleftharpoons & H^+ & + & H_2PO_4^- \\ 0.1(1-\alpha) & & 0.1\alpha & & 0.1\alpha \end{array}$$

$$K_1 = \frac{[H^+]\,[H_2PO_4^-]}{[H_3PO_4]} = \frac{0.1\,\alpha^2}{(1-\alpha)} = 7.5 \times 10^{-3}$$

Solving the quadratic equation as

$$0.1\,\alpha^2 + 7.5 \times 10^{-3}\,\alpha - 7.5 \times 10^{-3} = 0$$

We get $\alpha = 2.4 \times 10^{-2}$

$$\therefore \quad [H^+] = 2.4 \times 10^{-2}M,\ [H_2PO_4^-] = 2.4 \times 10^{-2}M$$

$$[H_3PO_4] = 0.1 - 2.4 \times 10^{-2} = 7.6 \times 10^{-2}M$$

Now, consider the second dissociation step:

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

Let the degree of dissociation of $H_2PO_4^-$ be β, so that

$$[H_2PO_4^-] = 2.4 \times 10^{-2} - \beta; \; [H^+] = 2.4 \times 10^{-2} + \beta; \; [HPO_4^{2-}] = \beta$$

$$K_2 = \frac{[HPO_4^{2-}]\,[H^+]}{[H_2PO_4^-]} = \frac{(2.4 \times 10^{-2} + \beta) \times \beta}{(2.4 \times 10^{-2} - \beta)}$$

It can be assumed that β is small and may be neglected when added or subtracted to 2.4×10^{-2}, so that

$$\beta = K_2 = 6.2 \times 10^{-8}\text{M}$$

$\therefore \; [HPO_4^{2-}] = 6.2 \times 10^{-8}\text{M}$ and others are the same, i.e.

$$[H^+] = 2.4 \times 10^{-2}\text{M}, \; [H_2PO_4^-] = 2.4 \times 10^{-2}\text{M}$$

Consider the third dissociation step

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$$

Let the degree of dissociation of HPO_4^{2-} be γ so that

$$[HPO_4^{2-}] = 6.2 \times 10^{-8} - \gamma; \; [PO_4^{3-}] = \gamma, \; [H^+] = 2.4 \times 10^{-2}\text{M}$$

$$K_3 = \frac{[PO_4^{3-}]\,[H^+]}{[HPO_4^{2-}]} = \frac{\gamma \times 2.4 \times 10^{-2}}{6.2 \times 10^{-8} - \gamma}$$

Neglecting γ from the denominator, i.e.,

$$6.2 \times 10^{-8} - \gamma \approx 6.2 \times 10^{-8}$$

$$\gamma = K_3 \times \frac{6.2 \times 10^{-8}}{2.4 \times 10^{-2}}$$

$$K_3 = 4.8 \times 10^{-13}$$

$$\therefore \quad \gamma = 4.8 \times 10^{-13} \times \frac{6.2 \times 10^{-8}}{2.4 \times 10^{-2}} = 1.24 \times 10^{-18}$$

$$[PO_4^{3-}] = 1.24 \times 10^{-8}\text{M}$$

Thus, the concentrations of various species in 0.1M H_3PO_4 solution are:

$$[H^+] = 2.4 \times 10^{-2}\text{M}; \; [H_2PO_4^-] = 2.4 \times 10^{-2}\text{M};$$

$$[HPO_4^{2-}] = 6.2 \times 10^{-8}\text{M}$$

$$[PO_4^{3-}] = 1.24 \times 10^{-18}\text{M}, \; [H_3PO_4] = 7.6 \times 10^{-2}\text{M}.$$

Dissociation Constants of Polyacidic Bases

Like polybasic acids, there exist polyacidic bases also, e.g.

$$[HONH_3CH_2CH_2NH_3OH]$$

The dissociation of these bases also takes place step by step.

14.5 DISSOCIATION OF WATER

Pure water is a very weak electrolyte and dissociates to a small extent as

$$H_2O \rightleftharpoons H^+ + OH^-$$

The ionization constant of water is

$$K = \frac{[H^+]\,[OH^-]}{[H_2O]}$$

Since the degree of dissociation of water is very small, the concentration of undissociated water may be taken to be constant (1000/18 = 55.56 mol l^{-1})

$$K\,[H_2O] = [H^+]\,[OH^-]$$

or $$K_w = [H^+]\,[OH^-]$$

where K_w is known as the *ionic product* of water. Its value is constant at a particular temperature and varies with change in temperature. At 25°C, the value of K_w is 1.0×10^{-14}. Thus, in water at 25°C,

$$[H^+] = [OH^-] = (1 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7}\ \text{mol}\ l^{-1}$$

An aqueous solution is acidic if $[H^+] > [OH^-]$ and basic if $[OH^-] > [H^+]$. For any aqueous solution of acid or base, the relationship between $[H^+]$ and $[OH^-]$ is

$$[H^+] = \frac{K_w}{[OH^-]}$$

It may be noted that for solutions of acids (up to 10^{-5}M), $[OH^-]$ is negligible, and similarly for bases (up to 10^{-5}M), $[H^+]$ is negligible.

14.6 THE pH SCALE

The pH of a solution is expressed as

$$pH = -\log a_{H^+}$$

where a_{H^+} is the activity of the hydrogen ion. But, for dilute solutions a_{H^+} is equal to its molarity so that

$$pH = -\log\,[H^+] = \log \frac{1}{[H^+]}$$

For neutral solution at 25°C, $[H^+] = 10^{-7}$ mol l^{-1}, so that

$$pH = -\log\,[10^{-7}] = 7$$

The pH value corresponding to acidic and basic solutions at 25°C will be less than and greater than 7, respectively.

In a similar manner,

$$pOH = -\log\,[OH^-]$$

pOH is related to pH as

$$pH + pOH = pK_w$$

where $pK_w = -\log K_w$. At 25°C, it is equal to 14. However, it may be noted that the acidic or basic nature of the solution is generally expressed in terms of pH.

Note This type of notation (pX) is also applied in the case of dissociation constants of acids and bases, e.g.

$$pK_a = -\log K_a \quad \text{and } pK_b = -\log K_b$$

where K_a and K_b are the dissociation constants of acids and bases.

EXAMPLE 14.6 Calculate the pH of the following solutions:

(a) 0.002M HCl

(b) Pure water at 25°C, $K_w = 1 \times 10^{-14}$

(c) 0.1M NH_4OH ($K_b = 1.8 \times 10^{-5}$)

(d) 0.01M CH_3COOH ($K_a = 1.85 \times 10^{-5}$)

(e) 0.015M NaOH

Solution

(a) 0.002M HCl

HCl is a strong acid and fully ionizes so that

$[H^+] = 0.002M = 2.0 \times 10^{-3}M$

$pH = -\log [H^+] = -\log (2 \times 10^{-3})$

$= -[-3 + 0.3010] = 2.6990$

(b) In pure water, $[H^+] = [OH^-]$

and $[H^+][OH^-] = K_w = 1 \times 10^{-14}$

$\therefore$ $[H^+]^2 = 1 \times 10^{-14}$ or $[H^+] = 1 \times 10^{-7}$

$pH = -\log [H^+] = -\log (10^{-7}) = 7$

(c) NH_4OH ionizes as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

If c is the initial concentration and α the degree of ionization, then

$$[NH_4OH] = c(1 - \alpha)\ ;\ [NH_4^+] = [OH^-] = c\alpha$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{(c\alpha)(c\alpha)}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

$$\therefore \quad \alpha = \sqrt{\frac{K_b}{c}}$$

Now, $K_b = 1.8 \times 10^{-5}$, $c = 0.1M$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 1.34 \times 10^{-2}$$

$\therefore$ $[OH^-] = c\alpha = 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3}$

Now, $[H^+][OH^-] = 1.0 \times 10^{-14}$

or $$[\mathrm{H}^+] = \frac{1.0 \times 10^{-14}}{[\mathrm{OH}^-]} = \frac{1.0 \times 10^{-14}}{1.34 \times 10^{-3}}$$

$$= 7.463 \times 10^{-12}$$

$$p\mathrm{H} = -\log\,[\mathrm{H}^+] = -\log\,(7.463 \times 10^{-12})$$
$$= -(-12 + 0.8729)$$
$$= 11.13$$

(d) Acetic acid ionizes as

$$\mathrm{CH_3COOH} \rightleftharpoons \mathrm{CH_3COO^-} + \mathrm{H^+}$$

If α is the degree of ionization and c the initial concentration, then

$$[\mathrm{CH_3COOH}] = c(1-\alpha),\ [\mathrm{H}^+] = [\mathrm{CH_3COO^-}] = c\alpha$$

Now, $$K_a = \frac{[\mathrm{CH_3COO^-}]\,[\mathrm{H}^+]}{[\mathrm{CH_3COOH}]} = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2$$

or $$\alpha = \sqrt{\frac{K_a}{c}}$$

Now, $K_a = 1.85 \times 10^{-5}$, $c = 0.01\mathrm{M}$

$$\alpha = \sqrt{\frac{1.85 \times 10^{-5}}{0.01}} = 4.30 \times 10^{-2}$$

$$[\mathrm{H}^+] = c\alpha = 0.01 \times 4.30 \times 10^{-2} = 4.30 \times 10^{-4}$$
$$p\mathrm{H} = -\log\,[\mathrm{H}^+] = -\log\,(4.30 \times 10^{-4})$$
$$= -(-4 + 0.6335)$$
$$= 3.37$$

(e) NaOH is a strong base and is completely ionized so that

$$[\mathrm{OH}^-] = 0.015\mathrm{M}$$

Now, $[\mathrm{H}^+]\,[\mathrm{OH}^-] = 1 \times 10^{-14}$

or $$[\mathrm{H}^+] = \frac{1 \times 10^{-14}}{[\mathrm{OH}^-]} = \frac{1 \times 10^{-14}}{0.015} = 6.67 \times 10^{-13}$$

$$p\mathrm{H} = -\log\,[\mathrm{H}^+] = -\log\,(6.67 \times 10^{-13})$$
$$= -(-13 + 0.8241)$$
$$= 12.18$$

EXAMPLE 14.7 A sample of blood has the pH value 7.4. What is the hydrogen ion concentration in it?

Solution $p\mathrm{H} = -\log\,[\mathrm{H}^+] = 7.4$

or $$\log\,[\mathrm{H}^+] = -7.4$$
$$[\mathrm{H}^+] = \text{antilog}\,(\bar{8}.6)$$
$$= 3.98 \times 10^{-8}\mathrm{M}$$

14.7 COMMON ION EFFECT

The dissociation of an acid or a base is much affected if one of the dissociated ions is added from a certain external source. For example, the degree of ionisation of acetic acid decreases considerably when H⁺ (say by adding HCl) or acetate ion (say by adding sodium acetate) are added to the solution.

Similarly, the ionization of ammonium hydroxide is considerably decreased by the addition of sodium hydroxide (OH^- ions) or ammonium chloride (NH_4^+ ions). These observations are in agreement with the Le Chatelier principle.

EXAMPLE 14.8 A solution is 0.1M in HCN and 0.1M in NaCN. Calculate the concentration of hydrogen and hydroxyl ions if the ionization constant of HCN is 7.2×10^{-10}.

Solution NaCN is a strong electrolyte. Therefore, on ionization, it gives 0.1M of CN^-. Cyanide ion is also produced by the ionization of HCN. Let the degree of ionization of HCN be α

$$\begin{array}{ccccc} HCN & \rightleftharpoons & H^+ & + & CN^- \\ c(1-\alpha) & & c\alpha & & c\alpha \end{array}$$

Thus,

$$[H^+] = c\alpha$$
$$[HCN] = c(1-\alpha)$$
$$[CN^-] = 0.1 + c\alpha$$

Now, $$K_a = \frac{[H^+]\,[CN^-]}{[HCN]} = \frac{c\alpha(0.1 + c\alpha)}{c(1-\alpha)}$$

Putting $K_a = 7.2 \times 10^{-10}$, $c = 0.1$,

$$7.2 \times 10^{-10} = \frac{0.1\alpha\,(0.1 + 0.1\alpha)}{0.1(1-\alpha)}$$
$$= \frac{0.1\alpha \times 0.1\,(1+\alpha)}{0.1\,(1-\alpha)}$$

If $\alpha \ll 1,\ 1 + \alpha \approx 1 \approx 1 - \alpha$

$$0.1\alpha = 7.2 \times 10^{-10}$$
$$\alpha = 7.2 \times 10^{-9}$$

and $$[H^+] = c\alpha = 0.1 \times 7.2 \times 10^{-9} = 7.2 \times 10^{-10}\ \text{mol}\ l^{-1}$$

and $$[OH^-] = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-10}} = 1.39 \times 10^{-5}\ \text{mol}\ l^{-1}$$

EXAMPLE 14.9 Find the concentration of hydroxyl ion in 0.1M ammonium hydroxide solution. What will be the change in concentration of hydroxyl ion when 5.35 g of NH_4Cl is added to 1000 ml of the solution (assume no change in volume, K_b for NH_4OH is 1.8×10^{-5}).

Solution NH_4OH ionizes as

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Let c be the initial concentration, and α the degree of dissociation, so that

$$NH_4OH = c(1-\alpha),\ [NH_4^+] = [OH^-] = c\alpha$$

and $$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = \frac{c\alpha^2}{(1-\alpha)} = \frac{0.1\alpha^2}{(1-\alpha)} = 1.8 \times 10^{-5}$$

Since α is very small so that $1 - \alpha \approx 1$

$$\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 13.4 \times 10^{-2}$$

$$[OH^-] = c\alpha = 0.1 \times 1.34 \times 10^{-2} = 1.34 \times 10^{-3}$$

When ammonium chloride is added

Amount of NH_4Cl added $= \frac{5.35}{53.5} = 0.1 \text{ mol } l^{-1}$

Since NH_4Cl is a strong electrolyte, on ionization, it gives 0.1M NH_4^+ ions. Let β be the degree of ionization of NH_4OH in the presence of NH_4Cl in the solution. Then,

$$\begin{array}{ccc} NH_4OH & \rightleftharpoons NH_4^+ & + \ OH^- \\ 0.1(1-\beta) & 0.1\beta & 0.1\beta \end{array}$$

$$[NH_4^+] = [NH_4^+] \text{ (from } NH_4Cl) + [NH_4^+] \text{ (from } NH_4OH)$$
$$= 0.1 + 0.1\beta$$

$$[OH^-] = 0.1\beta$$
$$[NH_4OH] = 0.1(1-\beta)$$

$$K_b = 1.8 \times 10^{-5} = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$
$$= \frac{(0.1 + 0.1\beta)(0.1\beta)}{0.1(1-\beta)}$$

Since β is small, neglecting β in comparison to one so that $1 - \beta \approx 1 + \beta \approx 1$, we get

$$1.8 \times 10^{-5} = 0.1\beta$$

or $$\beta = 1.8 \times 10^{-4}$$

or $$[OH^-] = c\beta = 0.1 \times 1.8 \times 10^{-4} = 1.8 \times 10^{-5}$$

Obviously, the concentration of OH^- ions has decreased in the presence of NH_4Cl, due to the common ion effect.

14.8 BUFFER SOLUTIONS AND BUFFER ACTION

Buffer solutions are those which resist change in *p*H on addition of small amounts of acids or bases, or on dilution of the solution.

The ability of buffer solutions to resist changes in *p*H value on addition of small amounts of acids or bases or on dilution is called *buffer action.*

Buffer solutions generally contain a weak acid and a salt of a weak acid, or a weak base and the salt of a weak base. For example, a solution containing equimolar quantities of CH_3COOH and CH_3COONa (acidic buffer), or a solution containing equimolar quantities of NH_4OH and NH_4Cl (basic buffer), etc.

For a buffer solution containing a weak acid and its salt,

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

This equation is called *Henderson's equation*. Similarly, the *p*H of a buffer solution containing a weak base and its salt is

$$pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]}$$

Buffer Capacity

Buffer capacity is defined as the number of moles (b) of acid (or base) added to one litre of solution to change the *p*H by unity.

$$\text{Buffer capacity} = \frac{db}{d[pH]}$$

i.e. it is the absolute value of the slope of the curve between moles of acid (or base) added to one litre of the solution and the *p*H of the solution.

EXAMPLE 14.10 Calculate the *p*H of a buffer solution containing 0.1M each of acetic acid and sodium acetate. What will be the change in *p*H on adding

(a) 0.01M of HCl to 1 litre of solution?

(b) 0.01M of NaOH to 1 litre of solution?

(Assume that no volume change occurs on the addition of HCl or NaOH).

Solution *p*H of the solution $= pK_a + \log \dfrac{[\text{sodium acetate}]}{[\text{acetic acid}]}$

$$pK_a = -\log(1.8 \times 10^{-5}) = -(-5 + 0.255) = 4.745$$

$$[CH_3COONa] = 0.1M, \quad [CH_3COOH] = 0.1M$$

$$\therefore \quad pH = 4.745 + \log \frac{0.1}{0.1} = 4.745$$

(a) When we add 0.01M of HCl to a litre of this solution, hydrogen ions from HCl will react with acetate ions to form un-ionized acetic acid. Therefore, the concentration of CH_3COO^- decreases by 0.01M and that of CH_3COOH increases by 0.01M. The concentrations become,

$$[CH_3COO^-] = 0.1 - 0.01 = 0.09M$$

$$[CH_3COOH] = 0.1 + 0.01 = 0.11M$$

$$pH = 4.745 + \log \frac{0.09}{0.11}$$

$$= 4.745 - 0.087 = 4.658$$

The change in *p*H is only $-$ 0.087

(b) On adding 0.01M of NaOH to a litre of the solution, acetic acid will react with OH^- ions to give acetate ions. The concentrations are now

$$[CH_3COO^-] = 0.1 + 0.01 = 0.11M$$
$$[CH_3COOH] = 0.1 - 0.01 = 0.09M$$
$$pH = 4.745 + \log \frac{0.11}{0.09}$$
$$= 4.745 + 0.087 = 4.832$$

Change in $pH = 0.087$

EXAMPLE 14.11 When 0.01 moles of NaOH are added to a buffer solution, its pH changes from 4.745 to 4.832. What is its buffer capacity?

Solution Buffer capacity $= \dfrac{\text{No. of moles of alkali added per litre}}{\text{Change in } pH}$

$$= \frac{0.01}{0.087} = 0.115$$

14.9 HYDROLYSIS OF SALTS

It is commonly observed that different salts, on dissolution in water, do not always form neutral solutions. The salts of strong acids and strong bases form neutral solutions. On the other hand, salts formed by strong acids and weak bases or weak acids and strong bases form acidic and basic solutions on dissolution in water. This is due to the fact that the ions of the salt react with water and give acidic or alkaline solutions. This phenomenon is called *hydrolysis*. It is defined as the reaction of the anion and (or) cation of the salt with water to produce an acidic or basic solution. It is the reverse of neutralization.

The equilibrium constant of such a reaction is called the *hydrolysis constant*. The hydrolysis equilibria and hydrolysis constants are given below:

$$A^- + H_2O \rightleftharpoons HA + OH^-; \qquad K_h = \frac{[HA]\,[OH^-]}{[A^-]} = \frac{ch^2}{1-h}$$

$$B^+ + H_2O \rightleftharpoons BOH + H^+; \qquad K_h = \frac{[BOH]\,[H_3O^+]}{[B^+]} = \frac{ch^2}{1-h}$$

The fraction of the total salt that has undergone hydrolysis at equilibrium is called the *degree of hydrolysis* (h). The hydrolysis constants and the degree of hydrolysis are related to the dissociation constants of the acid and base from which the salt is formed.

Hydrolysis of a Salt of a Weak Acid and a Strong Base

In this case, only the anion will undergo hydrolysis and will give free OH^- ions, thereby making the solution alkaline ($pH > 7$).

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

Here $$K_h = \frac{[HA]\,[OH^-]}{[A^-]} = \frac{[HA][OH^-][H^+]}{[A^-][H^+]} = \frac{K_w}{K_a}$$

and $$\frac{ch^2}{1-h} = \frac{K_w}{K_a} \text{ or } h \approx \sqrt{\frac{K_w}{K_a\,c}}$$

where c is the number of moles of the salt dissolved per litre of the solution. The pH of the solution is given by

$$pH = \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\, pK_a + \tfrac{1}{2} \log c$$

For example, the hydrolysis of solutions of sodium acetate, sodium cyanide, etc., are governed by this equation.

Hydrolysis of a Salt of a Strong Acid and a Weak Base

In this case, the cation will undergo hydrolysis to give H^+ (or H_3O^+) ions in solution, giving an acidic solution (pH < 7).

$$B^+ + H_2O \rightleftharpoons BOH + H^+$$

$$K_h = \frac{K_w}{K_b} = \frac{ch^2}{1-h} \text{ and } h = \sqrt{\frac{K_w}{K_b c}} \text{ for } h << 1$$

The pH of the solution is given by

$$pH = \tfrac{1}{2}\, pK_w - \tfrac{1}{2}\, pK_b - \tfrac{1}{2} \log c$$

For example, the hydrolysis of solutions of ammonium chloride, copper sulphate, etc., are governed by the above equation.

Hydrolysis of a Salt of a Weak Acid and a Weak Base

In this case, both the cation and anion undergo hydrolysis to the same or different extents. The resulting solution may be neutral, acidic or basic, depending upon the relative strengths of the acids and bases.

$$B^+ + A^- + H_2O \rightleftharpoons BOH + HA$$

$$K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{[BOH][HA][H^+][OH^-]}{[B^+][A^-][H^+][OH^-]} = \frac{K_w}{K_a K_b}$$

$$\text{Now, } K_h = \frac{h^2}{(1-h)^2} = \frac{K_w}{K_a\, K_b} \text{ and } h = \sqrt{\frac{K_w}{K_a\, K_b}}$$

The pH of the resulting solution is given by

$$pH = \tfrac{1}{2} pK_w + \tfrac{1}{2} pK_a - \tfrac{1}{2} pK_b$$

For example, hydrolysis of ammonium acetate, ammonium cyanide, etc.

Hydrolysis of a Salt of a Strong Acid and a Strong Base

In this case, neither the cation nor the anion undergo hydrolysis. The resulting solution is neutral.

EXAMPLE 14.12 Calculate (a) the hydrolysis constant (b) the degree of hydrolysis and (c) the pH of 0.1M solution of sodium acetate. The dissociation constant of CH_3COOH at room temperature is 1.8×10^{-5}.

Solution For sodium acetate, the hydrolysis reaction is

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

(a) The hydrolysis constant is

$$K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a}$$

$$K_w = 1.0 \times 10^{-14},\ K_a = 1.8 \times 10^{-5}$$

$$\therefore \quad K_h = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

(b) If c is the concentration and h the degree of hydrolysis,

$$K_h = \frac{ch^2}{1 - h}$$

If h is very small so that $1 - h \approx 1$

$$h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{5.56 \times 10^{-10}}{0.1}} = 7.42 \times 10^{-5}$$

Degree of hydrolysis is 0.00742%

(c) $[OH^-] = ch = 0.1 \times 7.42 \times 10^{-5} = 7.42 \times 10^{-6}$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{7.42 \times 10^{-6}} = 1.35 \times 10^{-9}$$

Now, $$\begin{aligned} pH &= -\log [H^+] = -\log (1.35 \times 10^{-9}) \\ &= -(-9 + 0.1303) \\ &= 8\ 87 \end{aligned}$$

Note pH can also be calculated from the relation,

$$pH = \tfrac{1}{2}\, pK_w + \tfrac{1}{2}\, pK_a + \tfrac{1}{2} \log c$$

$$pK_w = -\log (1 \times 10^{-14}) = 14$$

or $$pK_a = -\log (1.8 \times 10^{-5}) = -(-5 + 0.2553) = 4.745$$

$$\log c = \log 1 \times 10^{-1} = -1$$

$$\therefore\ pH = \tfrac{1}{2}(14) + \tfrac{1}{2}(4.745) - \tfrac{1}{2}(1) = 7 + 2.372 - 0.5 = 8.87$$

EXAMPLE 14.13 The pH of a 0.1M solution of ammonium chloride is 5.127. Calculate (a) the degree of hydrolysis (b) the hydrolysis constant and (c) the dissociation constant of the base.

Solution pH of the solution = 5.127

$$pH = -\log [H^+]$$

$$\log [H^+] = -pH = -5.127$$

$$\begin{aligned} [H^+] &= \text{antilog } (-5.127) = \text{antilog } (\bar{6}.873) \\ &= 7.46 \times 10^{-6} \end{aligned}$$

The hydrolysis reaction is

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

If h is the degree of hydrolysis and c the concentration, then

$$[H^+] = ch = 7.46 \times 10^{-6}$$

(a) Degree of hydrolysis, $h = \dfrac{7.46 \times 10^{-6}}{0.1} = 7.46 \times 10^{-5}$

(b) Hydrolysis constant, $$\begin{aligned} K_h &= \frac{ch^2}{1 - h} \\ &= 0.1 \times (7.46 \times 10^{-5})^2 \\ &= 5.56 \times 10^{-10} \end{aligned}$$

(c) Now, $K_h = \dfrac{[NH_4OH]\,[H^+]}{[NH_4^+\ ]} = \dfrac{K_w}{K_b}$

or $$K_b = \frac{K_w}{K_h} = \frac{1.0 \times 10^{-14}}{5.56 \times 10^{-10}} = 1.80 \times 10^{-5}$$

EXAMPLE 14.14 Calculate (a) the hydrolysis constant (b) the degree of hydrolysis and (c) the pH of a 0.1M NH_4CN solution at 25°C.

$$K_a = 4.0 \times 10^{-10},\ K_b = 1.8 \times 10^{-5}$$

Solution The hydrolysis reaction is

$$NH_4^+ + CN^- + H_2O \rightleftharpoons NH_4OH + HCN$$

(a) $$K_h = \frac{[NH_4OH]\,[HCN]}{[NH_4^+]\,[CN^-]} = \frac{K_w}{K_a\,K_b}$$

$$= \frac{1.0 \times 10^{-14}}{(4.0 \times 10^{-10}) \times (1.8 \times 10^{-5})} = 1.39$$

(b) If h is the degree of hydrolysis, then

$$K_h = \frac{ch \times ch}{c(1-h) \times c(1-h)} = \frac{h^2}{(1-h)^2}$$

or $$h = \sqrt{K_h} = \sqrt{1.39} = 1.18 \text{ for } h << 1$$

(c) The pH of the solution is given by

$$pH = \tfrac{1}{2}\,pK_w + \tfrac{1}{2}\,pK_a - \tfrac{1}{2}\,pK_b$$

$$\tfrac{1}{2}\,pK_w = \tfrac{1}{2}[-\log(1 \times 10^{-14})] = \tfrac{1}{2}[-(-14)] = 7$$

$$\tfrac{1}{2}\,pK_a = \tfrac{1}{2}\,[-\log\,(4 \times 10^{-10})] = \tfrac{1}{2}[\,-(-10 + 0.6020)] = 4.70$$

$$\tfrac{1}{2}\,pK_b = \tfrac{1}{2}\,[-\log\,(1.8 \times 10^{-5}] = \tfrac{1}{2}[\,-\,(\,-\,5 + 0.255)] = 2.37$$

$$pH = 7 + 4.70 - 2.37 = 9.33$$

14.10 ACID-BASE INDICATORS

Indicators are substances which change their colours within a certain range of pH. Generally, these are weak organic acids or bases, and have different colours in the un-ionized and ionized forms. For example, phenolphthalein is a weak acid. Its ionized form is pink while its un-ionized form is colourless (Fig. 14.1).

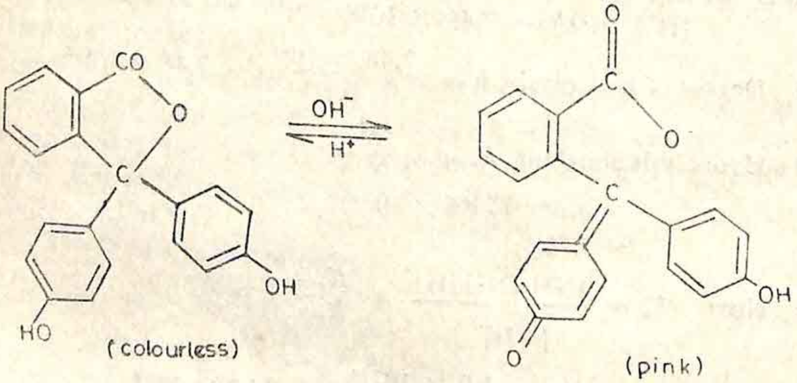


Fig. 14.1

Methyl orange is a weak base. Its ionized form is red and un-ionized form is yellow (Fig. 14.2).

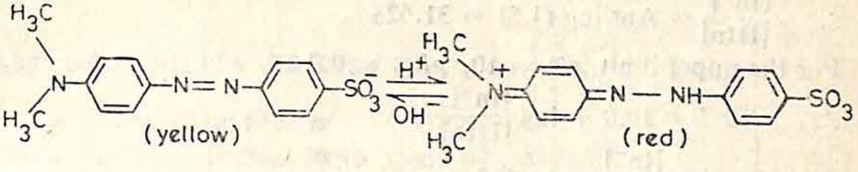


Fig. 14.2

In general, for acid-base indicators, equilibrium may be expressed as

$$HIn \rightleftharpoons H^+ + In^-$$

Its equilibrium constant is given by

$$K_{In} = \frac{[H^+][In^-]}{[HIn]}$$

so that $[H^+] = K_{In}\frac{[HIn]}{[I^-]}$ and $pH = pK_{In} + \log\frac{[In^-]}{[HIn]}$

In general, the intensity of the coloured solution depends upon the concentration of the colour-imparting species. For an indicator (say a weak acid whose pK_a is denoted by pK_{In}), the concentration of un-ionized indicator will be equal to the amount of its anion at $pH = pK_a$. At $pH = pK_{IN} - 1$, the ratio $[In^-]/[HIn]$ in the solution is 1/10, i.e. the un-ionized acid is ten times more and the colour of the un-ionized indicator will predominate.

On the other hand, at $pH = pK_{In} + 1$, the ratio of $[In^-]/[HIn]$ in the solution is 10/1, i.e. the ionized form is ten times greater and the solution has the colour characteristic of the In^- form.

In between the pH range $pK_{In} - 1$ to $pK_{In} + 1$, change of colour occurs. The function of the indicator is to give a sharp end point i.e. it must change its colour within the pH jump at the end point.

EXAMPLE 14.15 For phenolphthalein, $pK_{HIn} = 9.7$. The indicator can be used from pH 8.2 to 10. Calculate the ratio of $[In^-]/[HIn]$ for the lower and upper limits of the range.

Solution $pK_{In} = pH + \log\frac{[In^-]}{[HIn]}$

For the lower limit, $pH = 8.2$ and $pK_{In} = 9.7$

$$9.7 = 8.2 + \log\frac{[In^-]}{[HIn]}$$

$$\text{or } \log \frac{[\text{In}^-]}{[\text{HIn}]} = 9.7 - 8.2 = 1.5$$

$$\therefore \quad \frac{[\text{In}^-]}{[\text{HIn}]} = \text{Antilog } (1.5) = 31.623$$

For the upper limit, $p\text{H} = 10$, $pK_{\text{In}} = 9.7$

$$\therefore \quad 9.7 = 10.0 + \log \frac{[\text{In}^-]}{[\text{HIn}]}$$

$$\log \frac{[\text{In}^-]}{[\text{HIn}]} = -0.3$$

$$\frac{[\text{In}^-]}{[\text{HIn}]} = \text{antilog } (\bar{1}.7) = 0.501$$

14.11 ACID-BASE TITRATION CURVES

In acid–base titrations, successive amounts of a base are added to a solution of an acid (or *vice versa*) and the pH of the solution is noted after every addition. The plot of pH against the amount of alkali added is called a *titration curve*. The shape of the curve depends on the ionisation constants of the acid and base used in the titration.

Neutralization of a Strong Acid by a Strong Base

Initially, when alkali is added, the pH of the solution does not change much and the curve is almost flat (Fig. 14.3). At the end point there is a sudden jump in pH. This point is called the *equivalence point*. In this case, at the equivalence point, pH is 7. Slightly before and after this point, the pH changes from 3 to 11. Thus, any indicator which has a pH range within this interval can be used.

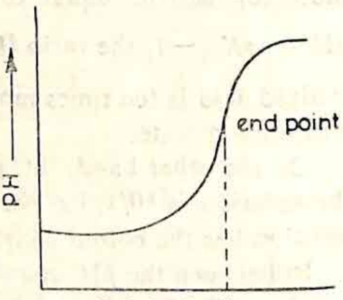


Fig. 14.3 *Titration curve of a strong acid and a strong base.*

Neutralization of a Weak Acid by a Strong Base

The pH curve is shown in Fig. 14.4. Initially the free hydrogen ions from the weak acid are neutralized by OH^- ions from the base and there is a relatively large chage in pH. The end point is detected by the inflection in the pH curve. However, the jump in pH is smaller than in case (a).

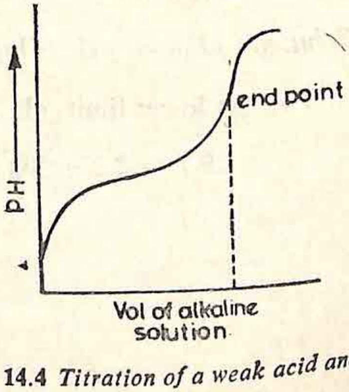


Fig. 14.4 *Titration of a weak acid and a strong base.*

Neutralization of a Weak Base with a Strong Acid

The curve will be as shown in Fig. 14.5.

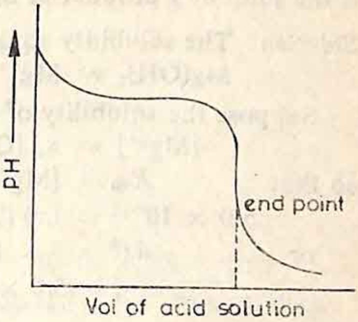


Fig. 14.5 *Titration curve of a weak base with a strong acid.*

14.12 SOLUBILITY PRODUCT

When a saturated solution of a sparingly soluble salt is in contact with some of the undissolved salt, there is an equilibrium between the dissolved ions and the undissociated solid salt. For example, the process of dissolution of AgCl may be expressed as:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

The equilibrium constant of the process is

$$K = \frac{[Ag^+]\,[Cl^-]}{[AgCl]}$$

The concentration of pure solid is constant so that [AgCl] may be combined with K to give a new constant called the *solubility product*, K_{sp}.

$$K\,[AgCl] = K_{sp} = [Ag^+]\,[Cl^-]$$

Thus, the solubility product may be defined as the product of ionic concentration in a saturated solution. When the salt, on dissolution, gives unequal number of cations and anions, then each concentration term is raised to the power equal to the number of times each ion occurs in the equation for its dissociation. For example,

$$Ag_2CrO_4\,(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}; \qquad K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$$

$$Al(OH)_3\,(s) \rightleftharpoons Al^{3+} + 3OH^-; \qquad K_{sp} = [Al^{3+}]\,[OH^-]^3$$

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}; \qquad K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$$

It must be emphasised that the solubility product at a given temperature is constant even for very soluble salts. In this case, activity is no longer equal to its concentration and activities must be used in place of the concentrations.

EXAMPLE 14.16 The solubility of CaF_2 (molar mass = 78) in water is 1.6×10^{-2} g l^{-1} at 20°C. Calculate the solubility product of CaF_2.

Solution

$$\text{Solubility in moles per litre} = \frac{1.6 \times 10^{-2}}{78} = 2.05 \times 10^{-4}$$

$$\text{Now,} \quad CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

$$\begin{aligned}\text{So that} \quad [Ca^{2+}] &= 2.05 \times 10^{-4}M \\ [F^-] &= 2 \times 2.05 \times 10^{-4} = 4.1 \times 10^{-4}M \\ K_{sp} &= [Ca^{2+}]\,[F^-]^2 \\ &= (2.05 \times 10^{-4})\,(4.1 \times 10^{-4})^2 \\ &= 3.45 \times 10^{-11}\end{aligned}$$

EXAMPLE 14.17 Calculate the solubility of $Mg(OH)_2$, in moles per litre, if the solubility product of $Mg(OH)_2$ is 5×10^{-12}.

Solution The solubility equilibrium is

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

Suppose the solubility of $Mg(OH)_2$ is x. Then,

$$[Mg^{2+}] = x, \ [OH^-] = 2x$$

so that $$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$5.0 \times 10^{-12} = (x)(2x)^2$$

or $$4x^3 = 5 \times 10^{-12}$$

$$x^3 = \frac{5.0 \times 10^{-12}}{4}$$

$$x = \left(\frac{5.0 \times 10^{-12}}{4}\right)^{1/3}$$

$$= (1.25)^{1/3} \times 10^{-4}$$

$$= 1.08 \times 10^{-4} \text{ mol } l^{-1}$$

14.13 SOLUBILITY PRODUCT AND PRECIPITATION OF SALTS

A substance will start precipitating as soon as the ionic product becomes greater than its solubility product. Knowing the solubility product of a salt, it is possible to predict whether, on mixing the solutions of its ions, precipitation will occur or not. This principle is of immense use in qualitative and gravimetric analysis, for the precipitation of cations or anions by adding sufficient amounts of the reagent.

EXAMPLE 14.18 Calculate $[Sr^{2+}]$ required to start the precipitation of stronium fluoride ($K_{sp} = 7.9 \times 10^{-11}$) from a solution that contains 0.01M F^- ions.

Solution

$$K_{sp} = [Sr^{2+}][F^-]^2$$

Precipitation will start when $[Sr^{2+}][F^-]^2$ becomes equal to K_{sp}. The $[Sr^{2+}]$ to start the precipitation is

$$[Sr^{2+}][0.01]^2 = 7.9 \times 10^{-11}$$

$$[Sr^{2+}] = \frac{7.9 \times 10^{-11}}{(0.01)^2} = 7.9 \times 10^{-7}\text{M}$$

$[Sr^{2+}]$ required to start precipitation $= 7.9 \times 10^{-7}$M

EXAMPLE 14.19 Predict whether there will be any precipitation on mixing 50 ml of 0.001M NaCl solution with 50 ml of 0.01M $AgNO_3$ solution. K_{sp} (AgCl) $= 1.5 \times 10^{-10}$.

Solution On mixing, the total volume becomes 100 ml. Thus, the concentrations of $AgNO_3$ and NaCl are decreased to half their values, i.e.

$$[AgNO_3] = \frac{0.01}{2} = 0.005\text{M}$$

$$[NaCl] = \frac{.001}{2} = 0.0005M$$

Now, $AgNO_3$ ionizes as

$$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$$

$$[Ag^+] = 0.005M = 5.0 \times 10^{-3}$$

and
$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$[Cl^-] = 0.0005M = 5.0 \times 10^{-4}$$

The ionic product is

$$[Ag^+]\,[Cl^-] = (5.0 \times 10^{-3}) \times (5.0 \times 10^{-4}) = 2.5 \times 10^{-6}$$

Thus, the ionic product is greater than K_{sp} (1.5×10^{-10}) and, therefore, precipitation of AgCl will occur.

EXAMPLE 14.20 The solubility products of silver halides are:

$K_{sp}\,(AgCl) = 1.7 \times 10^{-10}$, $K_{sp}\,(AgBr) = 5.0 \times 10^{-13}$ and $K_{sp}\,(AgI) = 8.5 \times 10^{-17}$

A solution contains 0.01M each of Cl^-, Br^- and I^- ions. Silver nitrate is gradually added to the solution. Assume that the addition of $AgNO_3$ does not change the volume.

(a) Calculate the $[Ag^+]$ required to start precipitation of the three ions.

(b) Which ion will precipitate first?

(c) What will be the concentration of this ion when the second ion starts precipitating?

(d) What will be the concentration of both the ions precipitated when the third ion starts precipitating?

Solution (a) The concentration of $[Ag^+]$ ion required to start precipitation can be calculated from the K_{sp} data:

For the chloride ion,

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.7 \times 10^{-10}}{0.01} = 1.7 \times 10^{-8}M$$

For the bromide ion,

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{5 \times 10^{-13}}{0.01} = 5 \times 10^{-11}M$$

For the iodide ion,

$$[Ag^+] = \frac{K_{sp}}{[I^-]} = \frac{8.5 \times 10^{-17}}{0.01} = 8.5 \times 10^{-15}M$$

(b) The $[Ag^+]$ required to precipitate I^- is minimum. Therefore, AgI will be precipitated first.

(c) After precipitation of AgI, the Br^- will be precipitated only when the $[Ag^+]$ becomes $5.0 \times 10^{-11}M$. Therefore, the concentration of remaining I^- is

$$[I^-] = \frac{K_{sp}\,(AgI)}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{5 \times 10^{-11}} = 1.7 \times 10^{-6}M$$

(d) The chloride ion, Cl^- will precipitate when the concentration of $[Ag^+]$ becomes 1.7×10^{-8}. Therefore, the concentrations of Br^- and I^- remaining in solution are.

$$[I^-] = \frac{K_{sp}\,(AgI)}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{1.7 \times 10^{-8}} = 5.0 \times 10^{-9} M$$

$$[Br^-] = \frac{K_{sp}\,(AgBr)}{[Ag^+]} = \frac{5 \times 10^{-13}}{1.7 \times 10^{-8}} = 2.94 \times 10^{-5} M$$

MISCELLANEOUS EXAMPLES

EXAMPLE 14.21 Calculate the pH of a 1.0×10^{-8} solution of HCl.

Solution One may be tempted to use the equation $pH = -\log [H^+]$ and find that pH equals 8. But this is not correct. It may be noted that, in very dilute acidic solution when H^+ concentrations from acid and the water are comparable, the concentration of H^+ from water cannot be neglected. Therefore,

$$[H^+]_{total} = [H^+]_{acid} + [H^+]_{water}$$

Since HCl is a strong acid and is completely ionized,

$$[H^+]_{HCl} = 1.0 \times 10^{-8}$$

The concentration of H^+ from water ionization is equal to the hydroxyl ion concentration from water, i.e.

$$[H^+]_{H_2O} = [OH^-]_{H_2O} = x \qquad \text{(say)}$$

$$[H^+]_{total} = 1.0 \times 10^{-8} + x$$

But $\quad [H^+]\,[OH^-] = 1.0 \times 10^{-14}$

$$(1.0 \times 10^{-8} + x)\,(x) = 1.0 \times 10^{-14}$$

$$x^2 + 10^{-8}\,x - 10^{-14} = 0$$

Solving for x, we get $x = 9.5 \times 10^{-8}$

$$[H^+] = 1.0 \times 10^{-8} + 9.5 \times 10^{-8} = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$$

Now, $pH = -\log [H^+] = -\log (1.05 \times 10^{-7})$

$$= -(-7 + 0.02)$$

$$= 6.98$$

EXAMPLE 14.22 The solubility product of AgCl is 1.5×10^{-10}. What weight of AgCl will be dissolved

(a) in 100 ml of water?

(b) in a solution containing 0.234 g of NaCl in 100 ml?

(c) in a solution containing 0.17 g of $AgNO_3$ in 100 ml?

Solution (a) Let the solubility of AgCl be x mol l^{-1}

$$AgCl \rightleftharpoons Ag^+ + Cl^-$$

$$[Ag^+] = x, \; [Cl^-] = x$$

$$K_{sp} = [Ag^+]\,[Cl^-] = x^2 = 1.5 \times 10^{-10}$$

$$x = (1.5 \times 10^{-10})^{\frac{1}{2}} = 1.225 \times 10^{-5} \text{ mol } l^{-1}$$

Solubility of AgCl in 100 ml $= (1.225\times10^{-5}\ \text{mol}\ l^{-1})\times(0.1\ l)\times$
$(143.5\ \text{g mol}^{-1}) = 1.75\times10^{-4}$ g

(b) The concentration of NaCl in the solution,

$$= \frac{0.234\times1000}{58.5\times100} = 0.04\ \text{mol}\ l^{-1}$$

Let the solubility of AgCl in the solution be y; so that $[\text{Cl}^-]=0.04+y$, $[\text{Ag}^+] = y$

$$K_{\text{sp}} = [\text{Ag}^+]\,[\text{Cl}^-] = (0.04+y)\,(y) = 1.5\times10^{-10}$$

y must be less than the solubility x determined above so that $0.04 + y \approx 0.4$

$\therefore\quad (0.04)\,y = 1.5\times10^{-10}$

or $\quad y = \dfrac{1.5\times10^{-10}}{0.04} = 3.75\times10^{-9}\ \text{mol}\ l^{-1}$

Solubility of AgCl in 100 ml solution $= 3.75\times10^{-9}\times0.1\times143.5$
$= 5.38\times10^{-8}$g

(c) The concentration of $AgNO_3$ in the solution,

$$= \frac{0.17\times1000}{170\times100} = 0.01\ \text{mol}\ l^{-1}$$

Let the solubility of AgCl in the solution be z, so that

$$[\text{Ag}^+] = 0.01 + z,\quad [\text{Cl}^-] = z$$

Now $\quad K_{\text{sp}} = [\text{Ag}^+]\,[\text{Cl}^-] = (0.01+z)\,z = 1.5\times10^{-10}$

$z \ll 1.225\times10^{-5}$ so that $0.01 + z \approx 0.01$

$(0.01)\,z = 1.5\times10^{-10}$

$\therefore\quad z = \dfrac{1.5\times10^{-10}}{0.01} = 1.5\times10^{-8}$

Solubility of AgCl in 100 ml solution
$= (1.5\times10^{-8}\ \text{mol}\ l^{1-})\times(0.1\ l)\times(143.5\ \text{g mol}^{-1})$
$= 2.15\times10^{-7}$ g

QUESTIONS

Numerical Problems

14.1 The dissociation constant of HCN at 25°C is 4.9×10^{-10} mol l^{-1}. Calculate the degree of dissociation of HCN in 0.1 and 0.01M solutions of HCN.

14.2 (SI Units) The dissociation constant of propionic acid at 298 K is 1.34×10^{-5}. What is the concentration of hydrogen ion in a 0.01 mol dm^{-3} solution of the acid? What is its degree of dissociation?

14.3 A 0.1M solution of formic acid (HCOOH) is 4.24% ionized at 25°C. Calculate the values of K_a and pK_a.

14.4 Calculate the H^+, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-} and H_3AsO_4 concentration in a 0.1 M solution of arsenic acid at 25°C, given that
$K_1 = 5.0\times10^{-3}$, $\quad K_2 = 8.3\times10^{-8}$ $\quad$ and $\quad K_3 = 6.0\times10^{-10}$ at 25°C.

14.5 The ionization constants of H_2S are : $K_1 = 1.1\times10^{-7}$ and $K_2 = 1.0\times10^{-14}$. What will be the concentrations of H^+, HS^- and S^{2-} when 0.1 moles of H_2S are dissolved in water to give one litre of solution? What will be the concentration of S^{2-} if the solution is 0.1 M in HCl also?

14.6 Calculate the pH of the following solutions at 25°C.
  (a) 0.4 g of NaOH dissolved in 2 dm^{-3} of water.
  (b) 0.01 M solution of glycolic acid, $K_a = 1.52 \times 10^{-4}$
  (c) 0.0001 M solution of aniline, $K_b = 3.8 \times 10^{-10}$

14.7 Calculate the value of pH and pOH of a 0.05 M solution of trimethylamine at 25°C ($K_b = 5.3 \times 10^{-5}$).

14.8 Calculate the pH of a solution obtained by mixing 50 ml of 0.1 M formic acid and 50 ml of 0.05 M sodium hydroxide (K_a for HCOOH $= 1.77 \times 10^{-4}$).

14.9 Calculate the pH of a solution obtained by mixing 100 ml of 1 M HCl with 100 ml of 0.6 M NaOH, with the resulting solution made up to 250 ml.

14.10 What will be the degree of ionization of ammonium hydroxide in a solution which is 0.05 M each in ammonium chloride and ammonium hydroxide (K_b for $NH_4OH = 1.8 \times 10^{-5}$)?

14.11 Calculate the percentage hydrolysis of sodium acetate in a 0.1 N solution at 25°C, assuming that the salt is completely dissociated.

$$[K_a\ (CH_3COOH) = 1.8 \times 10^{-5}]$$

14.12 Calculate the hydrolysis constant and degree of hydrolysis in
  (a) a 10^{-2} M solution of NH_4Cl ($K_b = 1.8 \times 10^{-5}$)
  (b) a 0.1 M solution of NaCN ($K_a = 7.24 \times 10^{-10}$)

14.13 Calculate (a) the hydrolysis constant (b) the degree of hydrolysis and (c) the pH of a solution of 0.1M CH_3COONH_4.

$$K_a\ (CH_3COOH) = K_b\ (NH_4OH) = 1.8 \times 10^{-5}$$

14.14 (SI Units) Calculate the pH of an aqueous solution of ethylamine containing 1.0×10^{-3} mol kg^{-1} of $C_2H_5NH_2$ at 298 K ($pK_b = 3.75$).

14.15 Calculate the [H^+] and [OH^-] at 25°C for the following solutions:
  (a) $p\text{H} = 4.65$ (b) $p\text{H} = 12.4$ (c) $p\text{OH} = 6.5$

14.16 The dissociation constant of acetic acid at 20°C is 1.8×10^{-5}. Calculate the pH of
  (a) a 0.25 M acetic acid solution
  (b) 0.25 M acetic acid solution containing 0.25 M sodium acetate
  (c) What will be the change in pH if we add 0.01 mole of HCl to a litre each of solutions (a) and (b) assuming no change in volume.

14.17 (a) Calculate the pH of a buffer solution which is 0.1 M of each NH_4OH and NH_4Cl ($K_b = 1.8 \times 10^{-5}$)
  (b) Calculate the change in pH on adding 0.01 mole of HCl and NaOH to a litre of the buffer solution.

14.18 Calculate the change in pH caused by dissolving 0.41 g of anhydrous sodium acetate (molar mass = 82) in 0.1 dm^3 of 0.1 mol dm^{-3} solution of acetic acid. (pK_a for $CH_3COOH = 4.74$).

14.19 Calculate the pH of a buffer solution containing 0.2 M NH_4OH and 0.25 M NH_4Cl at 25°C (K_b for $NH_4OH = 1.8 \times 10^{-5}$).

14.20 Calculate the solubility in mol l^{-1} for each of the following:
  (a) $BaSO_4 : K_{SP} = 7.5 \times 10^{-9}$
  (b) $Ag_2CrO_4 : K_{SP} = 1.7 \times 10^{-12}$
  (c) $MgF_2 : K_{SP} = 8 \times 10^{-8}$
  (d) $Al(OH)_3 : K_{SP} = 1.0 \times 10^{-33}$

14.21 Calculate the pH of a saturated solution of magnesium hydroxide if K_{SP} for $Mg(OH)_2$ is 8.9×10^{-12}.

14.22 The solubility product of lead iodate is 3.2×10^{-13}. Calculate the [Pb^{2+}] in a saturated solution of lead iodate in
  (a) pure water (b) 0.001 M $NaIO_3$ solution

14.23 (a) A solution is saturated with CaF_2. Calculate the concentration of Ca^{2+} ions (K_{sp} for CaF_2 is 3.95×10^{-10}).

(b) What will be the concentration of Ca^{2+} ions if the solution contains 0.1 M NaF.

14.24 When 0.001 mol of an acid are added to 50 ml of a buffer solution, its pH decreases by 0.05 units. What is its buffer capacity?

14.25 Calculate $[H^+]$ and $[OH^-]$ for a soft drink which has $pH = 4.70$.

14.26 Predict whether there will be any precipitation on mixing 30 ml of 0.001 M NaCl with 60 ml of 0.01 M $AgNO_3$ [K_{sp} (AgCl) $= 1.5 \times 10^{-10}$].

14.27 Calculate the $[Pb^{2+}]$ required to start the precipitation of $PbCl_2$ from a solution which contains 0.01 M chloride ions [K_{sp} ($PbCl_2$) $= 1.6 \times 10^{-5}$].

14.28 One litre of a solution contains 0.1 mol each of KI and KCl. Silver nitrate is gradually added to the solution from a burette.

(a) Which will be precipitated first, AgCl or AgI ?

(b) What will be the concentration of I^- ion in the solution when AgCl starts precipitating?

$$K_{sp}\,(AgCl) = 1.7 \times 10^{-10},\ K_{sp}\,(AgI) = 8.5 \times 10^{-17}$$

14.29 50 ml of 0.2 M $AgNO_3$ are added to 50 ml of 0.1 M NaBr solution. What will be the final concentration of Ag^+ and Br^- in the solution (K_{sp} for $AgBr = 5.0 \times 10^{-13}$)?

14.30 A solution contains 0.01 M Ag^+ and 0.02 M Ba^{2+} ions. A 0.01 M solution of Na_2CrO_4 is added gradually to it with constant stirring.

(a) At what concentration of Na_2CrO_4 will precipitation of Ag^+ and Ba^{2+} ions start?

(b) Which will precipitate first.

(c) What will be the concentration of the ion first precipitated when the precipitation of the second species starts?

Solubility products are:

$$K_{sp}\,(Ag_2CrO_4) = 2 \times 10^{-12}; \quad K_{sp}\,(BaCrO_4) = 8.0 \times 10^{-11}$$

QUIZ QUESTIONS

Type A: Multiple Choice

14.31 Which of the following can act both as a Brönsted acid and a Brönsted base?

(a) Na_2CO_3 (b) OH^-

(c) HCO_3^- (d) NH_3

14.32 The conjugate base of HCO_3^- is

(a) H_2CO_3 (b) H^+

(c) CO_2 (d) CO_3^{2-}

14.33 In the reaction

$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$

the conjugate acid-base pair is

(a) HCN, H_3O^+

(b) H_2O, CN^-

(c) CN^-, H_3O^+

(d) HCN, CN^-

14.34 Which of the following is not a Lewis bse?

(a) CN^- (b) $AlCl_3$

(c) ROH (d) NH_3

14.35 Which of the following statements is not correct regarding Lewis acids and bases?

(a) NH_3 and H_2O both behave as Lewis bases.
(b) Substances which can donate a pair of electrons are called Lewis bases.
(c) All Lewis bases are also Bronsted bases.
(d) Lewis bases must contain an atom having less than an octet of electrons.

14.36 In the reaction

$HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

the conjugate base of HNO_3 is

(a) H_2O
(b) H_3O^+
(c) NO_3^-
(d) H_3O^+ and NO_3^-

14.37 Which of the following acid-base reactions is according to Lewis classification?

(a) $(CH_3)_3\,N + BF_3 \rightleftharpoons (CH_3)_3\,N : BF_3$
(b) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
(c) $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$
(d) $H^+ + OH^- \rightleftharpoons H_2O$

14.38 The *p*H of a solution may be expressed as

(a) $pH = \log \dfrac{1}{[H^+]}$
(b) $pH = \log\,[H^+]$
(c) $pH = \dfrac{K_w}{[H^+]}$
(d) $pH = -\log 10^{[H^+]}$

14.39 The sum of *p*H and *p*OH in aqueous solution is equal to

(a) 7
(b) pK_w
(c) zero
(d) any number between 1 and 14

14.40 The dissociation constants of two weak acids are K_1 and K_2. The relative strengths of the two acids is given by

(a) $\dfrac{K_1}{K_2}$
(b) $\dfrac{K_1 + \sqrt{K_2}}{K_2 + \sqrt{K_1}}$
(c) $\left(\dfrac{K_1}{K_2}\right)^{1/2}$
(d) $\left(\dfrac{K_1}{K_2}\right)^{3/2}$

14.41. For a weak base, the concentration of OH^- ion at concentration *C* would be (dissociation constant $= K_b$)

(a) $\sqrt{\dfrac{K_b}{C}}$ (b) $\dfrac{K_b}{C}$
(c) $\sqrt{K_b \times C}$ (d) $\sqrt{K_b}/C$

14.42 Which of the following bases is the weakest ?

(a) $NH_4OH : K_b = 1.6 \times 10^{-5}$

(b) $C_6H_5NH_2 : K_b = 3.8 \times 10^{-10}$
(c) $C_2H_5NH_2 : K_b = 5.6 \times 10^{-4}$
(d) $C_9H_7N : K_b \quad = 6.3 \times 10^{-10}$

14.43 If c is the number of moles of acid present in one litre of solution and α is the degree of dissociation for the weak acid HA, then the dissociation constant is given by the expression

(a) $\dfrac{c^2\alpha^2}{1-\alpha}$

(b) $\dfrac{c\,(1-\alpha)}{\alpha^2}$

(c) $\dfrac{c\alpha^2}{1-\alpha}$

(d) $\dfrac{c\alpha^2}{(1-\alpha)^2}$

14.44 The value of pK_w at 25°C is
(a) 140
(b) 1×10^{-14}
(c) 14
(d) 0.014

14.45 Which of the following solutions has $pH = 11$?
(a) 1×10^{-11} M NaOH
(b) 1×10^{-3} M HCl
(c) 1×10^{-3} M NaOH
(d) 1×10^{3} M NaOH

14.46 The pK_a of an acid having ionisation constant 1×10^{-5} is
(a) 5 (b) −5
(c) 9 (d) −9

14.47 The pH of a buffer solution containing an acid and its salt is

(a) $pK_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

(b) $pK_a + \log \dfrac{[\text{acid}]}{[\text{salt}]}$

(c) $\frac{1}{2}pK_a - \log \dfrac{[\text{acid}]}{[\text{salt}]}$

(d) $\log pK_a + \log \dfrac{[\text{acid}]}{[\text{salt}]}$

14.48 In a mixture of a weak acid and its salt, the ratio of concentrations of salt to acid is increased ten fold. The pH of the solution
(a) decreases ten fold
(b) increases ten fold
(c) increases by one
(d) decreases by one

14.49 Which of the following will have the largest pH ?
(a) 0.1 N HCl
(b) 0.1 N CH_3COOH
(c) 0.1 N NaOH
(d) 0.01 N NaOH

14.50 The pH of a buffer solution containing a weak base and its salt can be related to pK_b as

(a) $pH = pK_b - \log \dfrac{[\text{salt}]}{[\text{base}]}$

(b) $pH = \frac{1}{2}pK_b - \frac{1}{2}\log \frac{[\text{salt}]}{[\text{base}]}$

(c) $pH = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]}$

(d) $pH = pOH - pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$

14.51 The pink colour of phenolphthalein in basic medium is due to the
(a) cationic form
(b) anionic form
(c) neutral form
(d) OH^- ions of the base

14.52 The Henderson equation relating the *p*H of a buffer solution to the proportion of salt, weak acid and pK_a may be verified by obtaining a linear plot with positive slope of
(a) pH and $\log \frac{[\text{acid}]}{[\text{salt}]}$
(b) pH and $\frac{[\text{acid}]}{[\text{salt}]}$
(c) pH and $\log \frac{[\text{salt}]}{[\text{acid}]}$
(d) pH and $\frac{[\text{salt}]}{[\text{acid}]}$

14.53 Which one of the following curves represents the graph of *p*H during the titration of NaOH and HCl ?

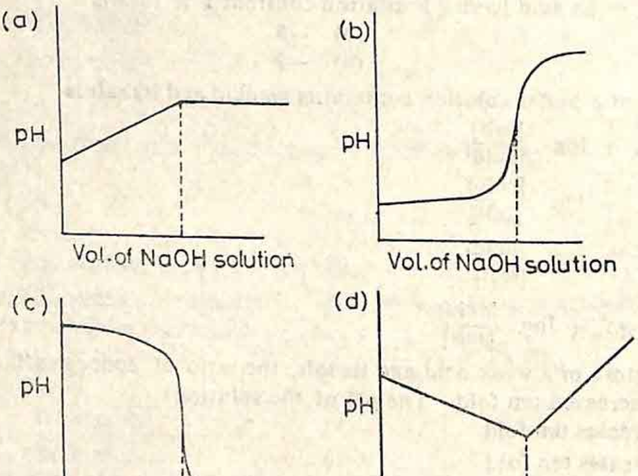


FIG. 14.6

14.54 The hydrolysis constant of the salt of a weak acid and weak base is (K_w = ionic product of water, K_a = dissociation constant of acid, K_b = dissociation constant of base)
(a) directly proportional to K_w, K_a and K_b
(b) directly proportional to K_a and inversely proportional to K_b.

(c) directly proportional to K_a and K_b and inversely proportional to K_w

(d) directly proportional to K_w and inversely proportional to K_a and K_b.

14.55 The solubility product for $Ca_3(PO_4)_2$ may be expressed as

(a) $[Ca^{2+}][PO_4^{3-}]$

(b) $[Ca^{2+}]^2[PO_4^{3-}]^3$

(c) $[Ca^{2+}]^3[PO_4^{3-}]^2$

(d) $[Ca^{2+}]^{3.2}[PO_4^{3-}]$

14.56 For a salt of a weak acid (dissociation constant K_a) and a weak base (dissociation constant K_b), the degree of hydrolysis h can be calculated from the relation

(a) $h = \dfrac{K_w}{K_a \times K_b}$

(b) $h = \sqrt{\dfrac{K_a}{K_b}}$

(c) $h = \left(\dfrac{K_a \times K_b}{K_w}\right)^{1/2}$

(d) $h = \left(\dfrac{K_w}{K_a \times K_b}\right)^{1/2}$

14.57 If the solubility of lithium sodium hexafluoroaluminate $Li_3Na_3(AlF_6)_2$ is x mol l^{-1}, then its solubility product is equal to

(a) $12x^3$	(b) $18x^3$
(c) x^8	(d) $2916x^8$

14.58 Which of the following acids is stronger than benzoic acid ($K_a = 6.3 \times 10^{-5}$)?

(a) A ($K_a = 1.67 \times 10^{-8}$)

(b) B ($pK_a = 6$)

(c) C ($pK_a = 4$)

(d) D ($K_a = 1.0 \times 10^{-5}$)

14.59 The pH of water is 7 at 25°C. If water is heated to 70°C, which of the following should be true?

(a) pH will decrease.

(b) pH will increase.

(c) pH will remain seven.

(d) Concentration of H^+ will increase but that of OH^- will decrease.

14.60 If x mol l^{-1} is the solubility of $KAl(SO_4)_2$, then K_{sp} is equal to

(a) x^3	(b) $4x^4$
(c) x^4	(d) $4x^3$

Type B: Multiple Choice (Numerical Problems)

14.61 An acid HA ionises as

$$HA \rightleftharpoons H^+ + A^-$$

The pH of 1 M solution of this acid is 6. The dissociation constant of this acid would be

(a) 1×10^{-6}

(b) 1×10^{-4}

(c) 1×10^{-3}

(d) 1×10^{-12}

14.62 Which of the following will have the largest *p*H value ?
(a) A solution containing 1×10^{-3} moles of KCl per litre.
(b) A solution containing 1×10^{-2} moles of HCl per litre.
(c) A solution containing 1×10^{-3} moles of NaOH per litre.
(d) Pure water

14.63 The *p*H of a solution having $[H^+] = 0.05$ M (log 5 = 0.6990) is
(a) 2.699 (b) 1.301
(c) 2.301 (d) 3.301

14.64 The dissociation constant of an acid at 25°C is 1.6×10^{-5}. What is the concentration of hydrogen ions in 0.01 M acid solution ?
(a) 4×10^{-2}
(b) 4×10^{-6}
(c) 4×10^{-3}
(d) 4×10^{-4}

14.65 The *p*H of a solution obtained by mixing 50 ml of 0.4 N HCl and 50 ml of 0.2 N NaOH is
(a) log 2 (b) 1
(c) − log (0.05) (d) 2

14.66 The ionization constant of dichloroacetic acid is 5×10^{-2}. Its pK_a value is (log 5 = 0.6990).
(a) 1.3010 (b) 3.3010
(c) 2.6990 (d) 1.6990

14.67 When 0.001 moles of an acid are added to 50 ml of a buffer solution, its *p*H decreases by 0.05 units. What is its buffer capacity ?
(a) 0.02 (b) 0.002
(c) 0.4 (d) 0.04

14.68 The dissociation constant of acetic acid at 25°C is 1.8×10^{-5}. The hydrolysis constant of sodium acetate is
(a) 1.8×10^{-5}
(b) 1.8×10^{-19}
(c) 5.55×10^{-10}
(d) 5.55×10^{4}

14.69 The *p*H of a buffer solution of 0.1 M CH_3COOH and 0.1 M CH_3COONa is (pK_a of $CH_3COOH = 4.745$)
(a) 4.745 (b) 3.745
(c) 5.745 (d) 3.255

14.70 What will be the hydrogen ion concentration of a solution obtained by mixing 500 ml of 0.2 M acetic acid and 500 ml of 0.4 M sodium acetate (dissociation constant of acetic acid = 1.8×10^{-5}) ?
(a) 1.8×10^{-5}
(b) 0.9×10^{-6}
(c) 9×10^{-6}
(d) 1.6×10^{-4}

14.71 Which of the following buffers containing NH_4OH and NH_4Cl has the highest *p*H value?

Conc. of NH_4OH	Conc. of NH_4Cl
(a) 0.50 mol l^{-1}	0.50 mol l^{-1}
(b) 0.10 mol l^{-1}	0.50 mol l^{-1}
(c) 0.50 mol l^{-1}	1.50 mol l^{-1}
(d) 0.50 mol l^{-1}	0.10 mol l^{-1}

14.72 A 0.1 M solution of a weak acid HA is 1% dissociated. The approximate value of the dissociation constant is

(a) 1×10^{-4} mol l^{-1}
(b) 0.1×10^{-2} mol l^{-1}
(c) 1×10^{-3} mol l^{-1}
(d) 0.1×10^{-4} mol l^{-1}

14.73 The *p*H of a 10^{-8} M solution of HCl is

(a) 8 (b) 6
(c) 0 (d) between 6 and 7

14.74 A buffer solution contains 0.2 mol of NH_4OH and 0.2 mol of NH_4Cl per litre. The pK_b of NH_4OH is 4.75. The *p*H of the buffer will be

(a) 4.75 (b) 5.75
(c) 9.25 (d) 2.25

14.75 The dissociation constant of a base is 1.5×10^{-10}. What is the degree of ionization of a 0.015 M solution of the base?

(a) 1×10^{-7}
(b) 1.0×10^{-6}
(c) 2.25×10^{-6}
(d) 1.0×10^{-4}

14.76 When a salt of a strong base and weak acid is hydrolysed, the resulting solution has

(a) $pH = 7$
(b) $pH = 0$
(c) $pH > 7$
(d) $pH < 7$

14.77 Four grams of sodium hydroxide have been dissolved in 10 *l* of the solution. The *p*H of the solution is

(a) 2 (b) 9
(c) 12 (d) 13

14.78 The dissociation constant of a weak acid is 7.2×10^{-10}. What is the concentration of hydrogen ions in a 0.072 M solution of the acid ?

(a) 0.36×10^{-4}
(b) 0.72×10^{-5}
(c) 7.2×10^{-12}
(d) 3.6×10^{-7}

14.79 The solubility product of AgCl is 1.0×10^{-10} at 25°C. The solubility in g l^{-1} is (molar mass of AgCl = 143.5)

(a) 1.43×10^{-5}
(b) 1.0×10^{-5}
(c) $1.0 \times 10^{-5}/143.5$
(d) 1.43×10^{-3}

14.80 If the solubility of CaF_2 in water at 20°C is 2.0×10^{-4} mol l^{-1}, the solubility product of CaF_2 is

(a) 4.0×10^{-8}
(b) 4.0×10^{-12}
(c) 3.2×10^{-8}
(d) 3.2×10^{-4}

Type C: True or False

14.81 At the equivalence point of an acid-base titration, the *p*H is always 7.

14.82 The term *p*H was introduced by Pauling.

14.83 A buffer solution is an example of the influence of the common ion effect.

14.84 After hydrolysis of a salt, the product [H^+] [OH^-] no longer equals K_w.

14.85 For the titration of a weak base with a strong acid, the equivalence point is at a *p*H less than 7.

14.86 The conjugate base of a strong acid is also strong.

14.87 All Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

14.88 In a solution of $AgNO_3$, [Ag^+] can be reduced by adding NaCl.

14.89 For precipitation to occur, the solubility product must be greater than the ionic product.

14.90 The *p*H of an acidic buffer containing [salt] / [acid] greater than one is more than pK_a of the acid.

Type D: Fill in the Blanks

14.91 The degree of dissociation of ammonium hydroxide ———— on addition of ammonium chloride.

14.92 The hydrolysis constant for the hydrolysis of a salt of a weak acid and strong base is ———— proportional to the dissociation constant of the acid.

14.93 NH_3 is classified as a Lewis ———— .

14.94 A solution which resists change in the hydrogen ion concentration on the addition of small amounts of acids or bases is called ———— .

14.95 When a strong acid is neutralised by an equal volume of weak base, the resulting solution will be ———— .

14.96 pK_b of a base is defined as ———— .

14.97 During titration of a weak acid and a strong base, the *p*H of the solution is ———— at the equivalence point.

14.98 The ionized form of phenolphthalein is ———— in colour while the unionized form is ———— .

14.99 The interaction of ions of a dissolved salt with H^+ and OH^- ions of water is known as ———— .

14.100 For precipitation to occur, the product must be ———— than the solubility product.

ANSWERS

Numerical Problems

14.1 7×10^{-5}, 2.21×10^{-4} *14.2* [H^+] $= 3.69 \times 10^{-4}$ M; $\alpha = 3.69 \times 10^{-2}$ *14.3* 1.88×10^{-4}, 3.726 *14.4* [H^+] $= 2.0 \times 10^{-2}$, [H_3AsO_4] $= 8.0 \times 10^{-2}$, [$H\,AsO_4^{2-}$] $= 8.3 \times 10^{-8}$, [AsO_4^{3-}] $= 2.49 \times 10^{-15}$ *14.5* [H^+] $= 1.05 \times 10^{-4}$; [HS^-] $= 1.05 \times 10^{-4}$, [S^{2-}] $= 1 \times 10^{-14}$; [S^{2-}] in the presence of HCl $= 1.1 \times 10^{-20}$ *14.6* (a) 11.70 (b) 2.91 (c) 7.79 *14.7* 11.21, 2.79 *14.8* 3.75 *14.9* 1.796 *14.10* 3.6×10^{-4} *14.11* 0.0075% *14.12* (a) 5.6×10^{-10}, 2.4×10^{-4}; (b) 1.38×10^{-5}, 1.17×10^{-2} *14.13* (a) 3.09×10^{-5} (b) 5.56×10^{-3} (c) 7 *14.14* (a) 2.25×10^{-5}, 4.46×10^{-10} (b) 3.98×10^{-13}, 2.51×10^{-2} (c) 3.2×10^{-8}, 3.12×10^{-7} *14.15* (a) 2.674 (b) 4.74 (c) 1.996, 4.56 *14.16* (a) 9.26 (b) 9.17 (c) 9.35 *14.17* 1.57 *14.18* 0.305 g *14.19* 9.16 *14.20* (a) 3.87×10^{-5} (b) 7.5×10^{-5} (c) 2.71×10^{-3} (d) 2.5×10^{-9} *14.21* 10.41 *14.22* (a) 4.3×10^{-5} (b) 8.0×10^{-8} *14.23* (a) 4.62×10^{-4} (b) 3.95×10^{-8} *14.24* 0.4 *14.25* 2×10^{-5}, 0.5×10^{-9} *14.26* ionic product is 2.2×10^{-6}, precipitation will occur *14.27* [Pb^{2+}] $= 0.16$ M *14.28* AgI will precipitate first; concentration of Ag^+ required for precipitation of AgI $= 8.5 \times 10^{-15}$, AgCl $= 1.7 \times 10^{-8}$; (b) 5×10^{-9} M *14.29* [Ag^+] $= 0.05$ M,

$[Br^-] = 1.0 \times 10^{-11}$ *14.30* (a) For Ag_2CrO_4, $[CrO_4^{2-}] = 2 \times 10^{-8}$. For $BaCrO_4$, $[CrO_4^{2-}] = 4 \times 10^{-9}$ (b) $BaCrO_4$ (c) 80% $BaCrO_4$ precipitated.

Quiz Questions

14.31 (c) *14.32* (d) *14.33* (d) *14.34* (b) *14.35* (d) *14.36* (c) *14.37* (a) *14.38* (a) *14.39* (b) *14.40* (c) *14.41* (c) *14.42* (b) *14.43* (c) *14.44* (c) *14.45* (c) *14.46* (a) *14.47* (a) *14.48* (c) *14.49* (c) *14.50* (c) *14.51* (b) *14.52* (c) *14.53* (b) *14.54* (d) *14.55* (c) *14.56* (d) *14.57* (d) *14.58* (c) *14.59* (a) *14.60* (b) *14.61* (d) *14.62* (c) *14.63* (b) *14.64* (d) *14.65* (b) *14.66* (a) *14.67* (c) *14.68* (c) *14.69* (a) *14.70* (a) *14.71* (d) *14.72* (d) *14.73* (d) *14.74* (c) *14.75* (d) *14.76* (c) *14.77* (c) *14.78* (b) *14.79* (d) *14.80* (d) *14.81* False : The equivalence point is at $pH = 7$ for strong acids and strong bases, but for others pH may be greater or lesser than 7 because the salt formed undergoes hydrolysis. *14.82* False *14.83* True *14.84* False *14.85* True *14.86* False *14.87* True *14.88* True *14.89* False *14.90* True *14.91* decreases *14.92* directly *14.93* base *14.94* buffer solution *14.95* acidic *14.96* $-\log K_b$ *14.97* greater than 7 *14.98* pink, colourless *14.99* hydrolysis *14.100* larger.

15

Electrochemical Cells

In an electrolytic cell, electrical energy is used to bring about a chemical reaction. The process may be reversed and electricity can be produced from chemical energy (released during a chemical reaction). Such devices, in which chemical energy is converted into electrical energy, are called electrochemical or galvanic cells. These cells are very important because of their many practical applications.

15.1 ELECTROCHEMICAL CELL

An electrochemical cell consists of two electrodes dipping into electrolyte solutions. These two electrodes are either dipping in the same solution or in different solutions separated by a salt bridge or porour material. Each compartment is called a half cell and the reaction occurring in each half cell is called a half cell reaction. Oxidation occurs at one electrode (anode) called oxidation half reaction and reduction occurs at the other (cathode) called reduction half reaction. The electrons released due to oxidation at the anode flow through the external wire to the cathode where reduction takes place. The overall cell reaction is the combination of the two half-cell reactions. For example, in the Daniell cell, the two electrodes of zinc and copper are dipped in $ZnSO_4$ and $CuSO_4$ solutions, respectively. The reactions are

$Zn(s) \rightleftharpoons Zn^{2+}(aq) + 2e^-$ Oxidation half reaction

$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$ Reduction half reaction

and $Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ Overall cell reaction

It may be noted that oxidation takes place at the anode and reduction at the cathode, both in the electrolytic and galvanic cells. However, in the two cases, the signs of the electrodes are opposite. In an electrolytic cell the anode is positively charged and the anions migrate to it and get oxidized, whereas in the galvanic cell the anode is negatively charged as the constituents of the electrode get oxidized leaving the electrode rich in electrons, i.e. the anode becomes negatively charged.

15.2 TYPES OF SINGLE ELECTRODES OR HALF CELLS

A single electrode consists of an electronic conductor (e.g. metal, gas adsorbed on metals, metal coated with sparingly soluble salts) in contact with an electrolytic conductor (electrolytic solution, fused salt, etc.)

Metal–Metal Ion Electrodes

This consists of a piece of metal dipped in a solution of its own ions. It is represented as $M^{n+} \mid M$ e.g. $Zn^{2+} \mid Zn$. The electrode reaction is

$$Zn^{2+} + 2e \rightleftharpoons Zn(s)$$

Gas Electrode

This consists of a gas bubbling over an inert metal dipping into a solution containing the corresponding ion. For example, the hydrogen electrode in which H_2 gas is bubbled over a platinized platinum electrode dipped in an acid solution. It is represented as $H^+ \mid H_2(p \text{ atm}) \mid Pt$. The reaction is

$$H^+ + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$

Metal-Metal Insoluble Salt Electrodes

These electrodes are prepared by coating a piece of metal with an insoluble salt of the same metal. For example, silver is coated with AgCl and dipped into a solution of Cl^- ions, represented as $Cl^- \mid AgCl \mid Ag$. The reaction is

$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

Inert Metal Electrodes

These consist of inert metal electrodes dipped in a solution containing ions with different oxidation states. For example, a platinum wire dipped in a solution of Fe^{2+} and Fe^{3+}, represented as $Fe^{3+}, Fe^{2+} \mid Pt$. The cell reaction is

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

Amalgam Electrodes

These consist of metal amalgams dipping in solutions of their ions. For example, lead amalgam dipping in a solution of Pb^{2+} ions. It is represented as $Pb(Hg)/Pb^{2+}$ The reaction is

$$Pb^{2+} + 2e^- \rightleftharpoons Pb \text{ (in Hg)}$$

15.3 ELECTROMOTIVE FORCE OF A CELL

The difference of potential which causes a flow of current from the electrode of higher potential to that of lower potential is called the electromotive force of the cell. This is commonly abbreviated as e.m.f. and expressed in volts. The e.m.f. can be interpreted in terms of the difference of electrode potentials by writing

e.m.f. of the cell = Reduction potential of the right-hand-side electrode − reduction potential of the left-hand-side electrode

i.e.,
$$\text{e.m.f.} = E_R - E_L \tag{15.1}$$

Note: This is in accordance with the thermodynamic convention that the change in any thermodynamic quantity is the difference between the final state (products) and the initial state (reactants).

Reduction potentials* give the tendency to gain electrons, *i.e.*

$$M^{n+} + ne^- \rightleftharpoons M(s)$$

e.g.
$$Zn^{2+} + 2e^- \rightleftharpoons Zn$$
$$AgCl + e^- \rightleftharpoons Ag + Cl^-$$

The e.m.f. of a cell cannot be measured with an ordinary voltmeter as the current drawn polarizes the electrodes. An unknown e.m.f. is opposed by another known e.m.f. until the two are equal, which is indicated by the galvanometer through a tap key (Poggendorff compensation method). However, these days VTVMs (vacuum tube voltmeters) are available, which draw very low currents and can be used for measuring the e.m.f. directly. A *p*H meter is actually a VTVM.

15.4 CONVENTIONS REGARDING CELL REACTIONS AND E.M.F.

An electrochemical cell consists of two electrodes. The e.m.f. of the cell depends upon the relative tendencies of oxidation and reduction at the two electrodes. The conventions regarding cells and cell reactions are :

1. In an electrochemical cell, oxidation occurs at the anode (or negative electrode), and reduction at the cathode (or positive electrode).
2. The cell is drawn in such a way that the reaction taking place at the left-hand-side electrode is oxidation and that on the right-hand-side electrode is reduction, i.e. in a cell the left-hand-side electrode acts as the negative electrode and the right-hand-side electrode acts as the positive electrode.
3. The e.m.f. of the cell is given as the electrode potential of the right-hand-side electrode (E_R) minus that of the left-hand-side

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*The electrode potential arises due to charge separation between the electrode and the solution. Its magnitude and sign depend upon the ease with which the ion (to which it is reversible) is reduced.

electrode (E_L), i.e.

$$E_{\text{cell}} = E_R - E_L$$

According to IUPAC convention, the electrode potential is always taken as the reduction potential for both electrodes.

4. The cell reaction can be determined by writing the oxidation and reduction reactions with equal numbers of electrons and then adding the two reactions. It may be noted that, to equalise the electrons in oxidation and reduction reactions, the half reactions are multiplied by suitable integers. But the electrode potentials do not change for these half-cell reactions.
5. If the e.m.f. of the cell ($E_R - E_L$) is positive, then the cell reaction is spontaneous in the forward direction, i.e. oxidation takes place at the LHS electrode and reduction at the RHS electrode.

Note: If the e.m.f. of the cell is negative, it means that reduction occurs at the left-hand electrode and oxidation at the right-hand electrode. For example, the e.m.f. of the cell

$$\text{Fe} \mid \text{Fe}^{2+}(a = 1) \parallel \text{Zn}^{2+}(a=1) \mid \text{Zn}$$

$$E^\circ_{\text{cell}} = E^\circ(\text{Zn}^{2+}, \text{Zn}) - E^\circ(\text{Fe}^{2+}, \text{Fe}) = -0.763 - (-0.440) = -0.323\text{V}$$

This means that the cell reaction

$\text{Fe} + \text{Zn}^{2+} (a = 1) \rightleftharpoons \text{Zn} + \text{Fe}^{2+}(a = 1)$ does not proceed.

But, if the positions of the electrodes are interchanged,

$$\text{Zn} \mid \text{Zn}^{2+} (a = 1) \parallel \text{Fe}^{2+}(a = 1) \mid \text{Fe}$$

so that $E^\circ_{\text{cell}} = -0.440 - (-0.763) = 0.323\text{V}$ and the reaction

$\text{Zn} + \text{Fe}^{2+} (a = 1) \rightleftharpoons \text{Zn}^{2+} (a = 1) + \text{Fe}$ is spontaneous.

Thus, for a spontaneous cell reaction ($E^\circ = +$ ve), the electrode with the higher electrode potential is written on the right-hand-side (acts as cathode and reduction occurs) and the one with the lower electrode potential is written on the left-hand side (acts as anode and oxidation occurs). The electrochemical cell may be represented as

$$\text{Zn} \mid \text{Zn}^{2+}(a = 1) \parallel \text{Fe}^{2+}(a = 1) \mid \text{Fe}$$

15.5 STANDARD ELECTRODE POTENTIAL

It is not possible to determine the potential of a single electrode because an electrochemical cell must contain two half cells suitably connected to each other. The problem can be solved by selecting an arbitrary reference electrode. For this purpose, a hydrogen electrode has been selected as the standard electrode and is assigned *zero potential*. It consists of a platinum foil coated with platinum black, dipped into an aqueous solution of H^+ ions of unit activity in which hydrogen gas at 1 atm pressure (taken as unit fugacity) is constantly bubbled. The potential of all other electrodes are measured with respect to this reference electrode.

(a) If, in a cell, the standard hydrogen electrode acts as an anode, i.e. oxidation occurs,

$$\tfrac{1}{2}H_2(g) \rightleftharpoons H^+(aq) + e^-$$

then reduction will occur at the other electrode and its electrode potential is positive. The e.m.f. of the cell is numerically equal to reduction potential of the other electrode, i.e.

$$E_{cell} = E_R - E_L$$
$$E_{cell} = E_R \qquad (E_L = 0)$$

(*b*) If the standard hydrogen electrode acts as a cathode, i.e. reduction occurs,

$$H^+(aq) + e^- \rightleftharpoons \tfrac{1}{2}H_2\,(g)$$

then the potential of the other electrode is negative.

$$E_{cell} = E_R - E_L$$
$$E_{cell} = -E_L \qquad (E_R = 0)$$

Since

$$E_{cell} = +ve$$
$$\therefore \quad E_L = -ve$$

All standard electrode potentials are taken as reduction potentials.

EXAMPLE 15.1 Write the half cell reactions and the overall cell reactions for the following electrochemical cells:

(a) $Pt \mid H_2\ (1\ atm) \mid HCl\ (a_1) \parallel Cu^{2+}\ (a_2) \mid Cu$

(b) $Cd \mid CdSO_4\ (a_1) \parallel SO_4^{2-}\ (a_2)\ Hg_2SO_4(s) \mid Hg(l)$

(c) $Pt \mid CO_2 \mid H_2C_2O_4,\ H^+(a_1) \parallel MnO_4^-,\ Mn^{2+},\ H^+ \mid Pt$

Solution (a) The cell reactions can be written by writing the oxidation half reaction (L.H.S. electrode) and reduction half reaction (R.H.S. electrode) as:

(a) Oxidation half reaction : $H_2(g) = 2H^+(a_1) + 2e^-$
Reduction half reaction : $Cu^{2+}(a_2) + 2e^- = Cu(s)$
Cell reaction : $Cu^{2+}(a_2) + H_2(g) = Cu(s) + 2H^+(a_1)$

(b) Oxidation half reaction : $Cd(s) = Cd^{2+}(aq) + 2e^-$
Reduction half reaction : $Hg_2SO_4(s) + 2e^- = 2Hg(l) + SO_4^{2-}(aq)$
Cell reaction : $Cd(s) + Hg_2SO_4(s) = Cd^{2+}(aq) + SO_4^{2-} + 2Hg(l)$

(c) Oxidation half reaction : $[H_2C_2O_4 = 2CO_2 + 2H^+ + 2e^-] \times 5$
Reduction half reaction : $[MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O] \times 2$
Cell reaction : $2MnO_4^- + 5H_2C_2O_4 + 6H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$

EXAMPLE 15.2 Calculate the standard e.m.f. for the following:

(a) $Zn \mid Zn^{2+}\ (a=1) \parallel Cu^{2+}(a=1) \mid Cu$

(b) $Cr \mid Cr^{3+}\ (a=1) \parallel Cu^{2+}(a=1) \mid Cu$

(c) $Pt \mid I^-(a=1),\ I_2 \parallel Fe^{2+}\ (a=1),\ Fe^{3+}\ (a=1) \mid Pt$

The standard electrode potentials are:

$E^\circ(Zn^{2+}, Zn) = -0.763$ V, $E^\circ(Cu^{2+}, Cu) = 0.337$ V,
$E^\circ(Cr^{3+}, Cr) = -0.774$ V, $E^\circ(I_2, I^-) = 0.535$ V,
$E^\circ(Fe^{3+}, Fe) = 0.771$ V.

Solution The e.m.f. of the cell is,

$$\overset{\circ}{E}_{\text{cell}} = \overset{\circ}{E}_R - \overset{\circ}{E}_L$$

(a) $Zn \mid Zn^{2+}\,(a=1) \parallel Cu^{2+}\,(a=1) \mid Cu$

$$\overset{\circ}{E}_R = E^\circ(Cu^{2+}, Cu) = 0.337 \text{ V}, \quad \overset{\circ}{E}_L = E^\circ(Zn^{2+}, Zn) = -0.763 \text{ V}$$

$$\overset{\circ}{E}_{\text{cell}} = 0.337 - (-0.763) = 1.1 \text{ V}$$

(b) $Cr \mid Cr^{3+}\,(a=1) \parallel Cu^{2+}\,(a=1) \mid Cu$

$$\overset{\circ}{E}_R = E^\circ(Cu^{2+}, Cu) = 0.337 \text{ V}, \quad \overset{\circ}{E}_L = E^\circ(Cr^{3+}, Cr) = -0.774$$

$$\overset{\circ}{E}_{\text{cell}} = 0.337 - (-0.774) = 1.111 \text{ V}$$

(c) $Pt \mid I^-\,(a=1), I_2 \parallel Fe^{2+}\,(a=1), Fe^{3+}\,(a=1) \mid Pt$

$$\overset{\circ}{E}_R = E^\circ(Fe^{3+}, Fe^{2+}) = 0.771 \text{ V}, \quad \overset{\circ}{E}_L = E^\circ(I_2, I^-) = 0.535 \text{ V}$$

$$\overset{\circ}{E}_{\text{cell}} = 0.771 - 0.535 = 0.236 \text{ V.}$$

15.6 NERNST EQUATION: DEPENDENCE OF E.M.F. ON CONCENTRATION

The e.m.f. of a cell depends on both the standard e.m.f. (E°) as well as the activities (concentrations) of the species involved in the cell reaction. For a general reaction of the type

$$aA + bB \rightleftharpoons lL + mM$$

the e.m.f. of the cell is given by the equation

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_L)^l\,(a_M)^m}{(a_A)^a\,(a_B)^b} \tag{15.2}$$

where a_A, a_B, a_L and a_M are the activities of the species A, B, L and M respectively, n is the number of electrons transferred if the chemical equation is expressed in two half-cell reactions, R is the gas constant and F is the Faraday (96500 C). Here E° represents the *standard e.m.f.* and is the e.m.f. of the cell when all the reactants and products are in their standard states (unit activity). This equation is called the Nernst equation

Equation (15.2) may be written as

$$E = E^\circ - \frac{2.303\,RT}{nF} \log \frac{(a_L)^l\,(a_M)^m}{(a_A)^a\,(a_B)^b} \tag{15.3}$$

Substituting the values of constants ($R = 8.314$ J K^{-1} mol^{-1}, $T = 298$ K, $F = 96500$ C mol^{-1}), the above equation becomes

$$E = E^\circ - \frac{0.0591}{n} \log \frac{(a_L)^l\,(a_M)^m}{(a_A)^a\,(a_B)^b} \tag{15.4}$$

If the solutions behave ideally, the activities* may be replaced by concentrations, i.e.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[L]^l\,[M]^m}{[A]^a\,[B]^b} \tag{15.5}$$

EXAMPLE 15.3 What will be the e.m.f. of the cell

$$Zn \mid Zn^{2+}\,(a = 0.01) \parallel Fe^{2+}\,(a = 0.005) \mid Fe$$

given that E° (Zn^{2+}, Zn) = −0.763 V and E° (Fe^{2+}, Fe) = −0.44 V

Solution The half cell reactions are

$$Zn\,(s) \rightleftharpoons Zn^{2+} + 2e^-$$
$$Fe^{2+} + 2e^- \rightleftharpoons Fe(s)$$

Cell reaction, $Zn(s) + Fe^{2+} \rightleftharpoons Fe(s) + Zn^{2+}$

The standard e.m.f. of the cell

$$E^\circ = E^\circ\,(Fe^{2+}, Fe) - E^\circ(Zn^{2+}, Zn)$$
$$= -0.440 - (-0.763) = 0.323 \text{ V}$$

The cell e.m.f. is

$$E = E^\circ - \frac{0.0591}{n} \log \frac{a_{(Zn^{2+})}}{a_{(Fe^{2+})}}$$

$$n = 2,\ E^\circ = 0.323 \text{ V},\ a_{(Zn^{2+})} = 0.01,\quad a_{(Fe^{2+})} = 0.005$$

$$E = 0.323 - \frac{0.0591}{2} \log \frac{0.01}{0.005}$$
$$= 0.323 - 0.009$$
$$= 0.314 \text{ V}.$$

Thus, e.m.f. of the cell is 0.314 V.

EXAMPLE 15.4 Consider the cell reaction

$$Ag(s) + Cu^{2+}(a = 0.48) + Br^-(a = 0.40) = AgBr(s) + Cu^+(a = 0.32)$$

given that the standard e.m.f. of the cell with the above cell reaction at 298 K is 0.058 V.

(a) Write the reactions occurring at the anode and cathode.
(b) Construct the cell.
(c) Calculate the e.m.f. of the cell.

Solution (a) At the anode (oxidation occurs).

$$Ag(s) + Br^- \rightleftharpoons AgBr(s) + e^-$$

At the cathode (reduction occurs).

$$Cu^{2+} + e^- \rightleftharpoons Cu^+$$

---

*The electrode potential depends upon the activity of the ions towards which it is reversible. However, in case of dilute solutions, activities are equal to the concentrations (M).

(b) The cell may be represented as
$Ag \mid AgBr(s), Br^-(a=0.40) \parallel Cu^+(a=0.32), Cu^{2+}(a=0.48) \mid Pt$

(c) The e.m.f. of the cell is given by

$$E = E^\circ - \frac{0.0591}{1} \log \frac{[a_{(Cu^+)}]}{[a_{(Cu^{2+})}][a_{(Br^-)}]}$$

$$= 0.058 - \frac{0.0591}{1} \log \frac{0.32}{0.48 \times 0.40}$$

$$= 0.058 - 0.013$$

$$= 0.045 \text{ V}$$

Thus, e.m.f. of the cell = 0.045 V.

15.7 THERMODYNAMICS AND E.M.F.

Thermodynamic functions, such as free energy, entropy and enthalpy changes, for cell reactions can be calculated from the e.m.f. and its temperature dependence.

Free energy change

$$\Delta G = -nFE \tag{15.6}$$

Differentiating ΔG with respect to temperature at constant pressure, we get

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -nF\left(\frac{\partial E}{\partial T}\right)_p$$

But $\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S$

$$\therefore \quad \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p \tag{15.7}$$

Now $\Delta G = \Delta H - T\Delta S$ or $\Delta H = \Delta G + T\Delta S$

So that $\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p = nF\left[T\left(\frac{\partial E}{\partial T}\right)_n - E\right]$ (15.8)

Note: Half cells and cell reactions can be written with different numbers of electrons. It must be appreciated that the cell potential remains unchanged whereas free energy changes. For example, in the cell

$Zn \mid Zn^{2+} (a = 0.01) \parallel Ag^+ (a = 0.005) \mid Ag$

cell reactions may be written as

$$\left.\begin{array}{l} Zn \rightleftharpoons Zn^{2+} + 2e^- \\ 2Ag^+ + 2e^- \rightleftharpoons 2Ag \end{array}\right\} \quad \begin{array}{c} Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag \\ \text{Case I} \end{array}$$

or

$$\left.\begin{array}{l} \frac{1}{2}Zn \rightleftharpoons \frac{1}{2}Zn^{2+} + e^- \\ Ag^+ + e^- \rightleftharpoons Ag \end{array}\right\} \quad \begin{array}{c} \frac{1}{2}Zn + Ag^+ \rightleftharpoons \frac{1}{2}Zn^{2+} + Ag \\ \text{Case II} \end{array}$$

or

$$\left.\begin{aligned} 2Zn &\rightleftharpoons 2Zn^{2+} + 4e^- \\ 4Ag^+ + 4e^- &\rightleftharpoons 4Ag \end{aligned}\right\} \quad \underset{\text{Case III}}{2Zn + 4Ag^+ \rightleftharpoons 2Zn^{2+} + 4Ag}$$

According to Nernst equation

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[a_{(Zn^{2+})}]^{n_{(Zn^{2+})}}}{[a_{(Ag^+)}]^{n_{(Ag^+)}}}$$

where $n_{(Zn^{2+})}$ and $n_{(Ag^+)}$ represent the number of ions of zinc and silver, respectively. If we put these variables according to the overall reactions:

$$E = \underset{\text{Case I}}{E^\circ - \frac{RT}{2F}\ln\frac{[a_{(Zn^{2+})}]}{[a_{(Ag^+)}]^2}} = \underset{\text{Case II}}{E^\circ - \frac{RT}{F}\ln\frac{[a_{(Zn^2}]^{\frac{1}{2}}}{[a_{(Ag^+)}]}}$$

$$= \underset{\text{Case III}}{E^\circ - \frac{RT}{4F}\ln\frac{[a_{(Zn^{2+})}]^2}{[a_{(Ag^+)}]^4}}$$

Thus, e.m.f. in all three cases is the same. However, free energies, given by the relation $\Delta G = -nFE$, are different in all three cases. This is because e.m.f. is an intensive quantity (difference of potentials) whereas ΔG is an extensive quantity.

Example 15.5 The standard e.m.f. of the cell

Pt | H_2 (1 atm), H^+ ($a = 1$) ‖ KCl ($a = 1$), AgCl | Ag at 298 K is 0.223 V. The temperature coefficient of the e.m.f. at constant pressure has been found to be -0.65 mVK^{-1}.

(a) Write the cell reaction for the cell.

(b) Calculate ΔG°, ΔS° and ΔH° for the cell reaction.

Solution

(a) Oxidation half reaction : $\frac{1}{2}H_2(g) \rightleftharpoons H^+\ (a = 1) + e^-$

Reduction half reaction : $AgCl + e^- \rightleftharpoons Ag + Cl^-\ (a = 1)$

Cell reaction : $AgCl(s) + \frac{1}{2}H_2(g) \rightleftharpoons Ag(s) + H^+(a=1) + Cl^-(a = 1)$

(b) The Gibbs free energy change for the reaction at 298 K

$$\Delta G^\circ = -nFE^\circ$$

$$n = 1,\ F = 96500\ \text{C mol}^{-1},\ E^\circ = 0.223\ \text{V}$$

$$\begin{aligned} \therefore\ \Delta G^\circ &= -(1)\times(96500\ \text{C mol}^{-1})\times(0.223\ \text{V}) \\ &= -21.520\times 10^3\ \text{C V mol}^{-1} \\ &= -21.520\ \text{kJ mol}^{-1} \qquad [\text{C.V.} = \text{J}] \end{aligned}$$

$$\Delta S^\circ = nF\left(\frac{\partial E^\circ}{\partial T)}\right)_p$$

The temperature coefficient of the e.m.f. at constant pressure

$$\left(\frac{\partial E}{\partial T}\right)_p = -0.65 \text{ m V K}^{-1} = -0.65\times 10^{-3} \text{ V K}^{-1}$$

$$\begin{aligned}\text{Thus, } \Delta S^\circ &= (1)\times(96500 \text{ C mol}^{-1})\times(-0.65\times10^{-3} \text{ V K}^{-1})\\ &= -62.7 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Now, } \Delta H^\circ &= \Delta G^\circ + T\Delta S^\circ\\ &= -21.52 \text{ kJ mol}^{-1} + (298 \text{ K})\times(-62.7\times10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})\\ &= -21.520 - 18.685\\ &= -40.205 \text{ kJ mol}^{-1}.\end{aligned}$$

15.8 EQUILIBRIUM CONSTANT AND E.M.F.

The e.m.f. of the cell may be used to calculate the equilibrium constant for the cell reaction.

$$-\Delta G^\circ = RT \ln K = nFE^\circ \tag{15.9}$$

$$\therefore \quad RT \ln K = nFE^\circ$$

$$\text{or} \quad \log K = \frac{nFE^\circ}{2.303\ RT}$$

EXAMPLE 15.6 Calculate the equilibrium constant for the reaction

$$2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$$

at 298 K, given that

$$E^\circ(I_2, I^-) = 0.536 \text{ V and } E^\circ(Fe^{3+}, Fe^{2+}) = 0.771 \text{ V}$$

Solution The cell reaction can be written as:

$2I^- \rightleftharpoons I_2 + 2e^-$ at anode (oxidation)

$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$ at cathode (reduction)

$$\begin{aligned}\text{So that e m.f. } &= E_R \quad E_L\\ &= E^\circ(Fe^{3+}, Fe^{2+}) - E^\circ(I_2, I^-)\\ &= 0.771 - 0.536\\ &= 0.235 \text{ V}\end{aligned}$$

The equilibrium constant K for the reaction

$$2Fe^{3+} + 2I^- \rightleftharpoons 2Fe^{2+} + I_2$$

is given by the relation

$$\log K = \frac{nFE^\circ}{2.303\ RT}$$

$n = 2$, $F = 96500$ C mol^{-1}, $E^\circ = 0.235$ V, $R = 8.314$ J K^{-1} mol^{-1}, $T = 298$ K

$$\begin{aligned}\log K &= \frac{2\times(96500 \text{ C mol}^{-1})\times(0.235 \text{ V})}{2.303\times(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\times(298 \text{ K})}\\ &= 7.95\\ K &= 8.9\times10^7\end{aligned}$$

15.9 *p*H MEASUREMENTS

It is possible to construct a cell in which the potential at one of the electrode (reference electrode) remains constant while that of the other electrode (indicator electrode) depends on the activity of the H^+ ions in the solution in which it dips. This helps to determine the activity of the hydrogen ion or the *p*H of the solution.

In addition to the hydrogen electrode, any electrode whose potential depends upon activities of H^+ or OH^- ions, can be used to measure *p*H.

The Hydrogen Electrode

The electrode potential of the hydrogen electrode involving the reaction

$$H^+ [a_{(H^+)}] + e^- \rightleftharpoons \tfrac{1}{2}H_2(g)$$

is

$$E = -\frac{RT}{F} \ln \frac{[f_{(H_2)}]^{\frac{1}{2}}}{[a_{(H^+)}]}$$

If the pressure of the gas is 1 atm (i.e. $f = 1$),

$$E = -\frac{RT}{F} \ln \frac{1}{a_{(H^+)}} = \frac{2.303\ RT}{F} \log [a_{(H^+)}]^{-1}$$

$$= -\frac{2.303\ RT}{F}\ p\text{H}$$

*p*H can be determined by coupling the hydrogen electrode with a reference electrode [say calomel electrode, KCl (sat. soln), $Hg_2Cl_2(s)$ | Hg]. The cell is

Reference electrode ‖ $H^+ [a_{(H^+)}]$ | H_2 (1 atm) | Pt

$$E_{\text{cell}} = -\frac{2.303\ RT}{F}\ p\text{H} - E_{\text{reference}}$$

At 298 K, $E_{\text{cell}} = -0.0591\ p\text{H} - E_{\text{reference}}$

$$\therefore\ p\text{H} = \frac{E_{\text{reference}} - E_{\text{cell}}}{0.0591}$$

Generally, a calomel electrode is used as a reference electrode. This consists of mercury, solid mercurous chloride and a solution of potassium chloride. It may be represented as KCl (solution) | $Hg_2Cl_2(s)$ | Hg. The concentration of the solution is either 0.1 mol dm^{-3}, 1 mol dm^{-3} or saturated. The reactions taking place at the electrode, if it involves oxidation or reduction, are, respectively,

$$2Hg(l) + 2Cl^- \rightleftharpoons Hg_2Cl_2(s) + 2e^- \quad \text{(oxidation)}$$
$$Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^- \quad \text{(reduction)}$$

The Quinhydrone Electrode

Quinhydrone is an equimolar mixture of quinone and hydroquinone, At a Pt electrode the following equilibrium takes place:

$$\underset{\text{Quinone}}{C_6H_4O_2}+2H^+ +2e^- \rightleftharpoons \underset{\text{Hydroquinone}}{C_6H_6O_2}$$

The reduction potential of the electrode is

$$E_{(Q,\,QH_2,\,H^+)} = E^\circ - \frac{RT}{2F}\ \ln \frac{a_{(QH_2)}}{[a_{(Q)}][a_{(H^+)}]^2}$$

In solutions, the activities of Q and QH_2 are constant so that

$$E_{(Q,\,QH_2,\,H^+)} = E^\circ - \frac{2.303\ RT}{F}\, p\mathrm{H}$$

where $E^\circ_{(Q,\,QH_2,\,H^+)}$ has a value of 0.6996 V.

For a cell,

Reference electrode ‖ $H^+ [a_{(H^+)}]$ Q, QH_2 | Pt

$$E_{cell} = E^\circ_{(Q,\,QH_2,\,H^+)} - \frac{2.303\ RT}{F}\ p\mathrm{H} - E_{reference}$$

$$\therefore\quad p\mathrm{H} = \frac{E^\circ_{(Q,\,QH_2,\,H^+)} - E_{reference} - E_{cell}}{2.303\ RT/F}$$

$$\text{At 298 K, } p\mathrm{H} = \frac{E^\circ_{(Q,\,QH_2,\,H^+)} - E_{reference} - E_{cell}}{0.0591}$$

The Glass Electrode

When two solutions of different pH are separated by a glass membrane, the potential across the membrane depends upon the difference in pH of the two solutions This type of electrode consists of a bulb made of a special glass containing 0.1 N hydrochloric acid and a silver–silver chloride electrode. The glass electrode is immersed in the solution whose pH is to be measured.

Ag | AgCl(s), 0.1 mol dm^{-3} HCl | glass | soln of unknown pH

The electrode potential of the glass electrode is

$$E_G = E^\circ_G - \frac{RT}{F}\ \ln a_{(H^+)} = E^\circ_G + \frac{2.303\ RT}{F}\ p\mathrm{H}$$

When coupled with the reference electrode, the cell is

Ag | AgCl(s), 0.1 mol dm^{-3}HCl | glass | solution $[a_{(H^+)}]$ ‖ Reference electrode

$$E_{cell} = E_{reference} - E_G$$

$$= E_{reference} - E^\circ_G - \frac{2.303\ RT}{F}\ p\mathrm{H}$$

$$p\mathrm{H} = \frac{E_{reference} - E^\circ_G - E_{cell}}{2.303\ RT/F}$$

$$\text{At 298 K, } p\mathrm{H} = \frac{E_{reference} - E^\circ_G - E_{cell}}{0.0591}$$

Specific Ion Electrodes

In recent years, a number of electrodes have been developed whose potentials depend on the ratio of activities of a particular ion across suitable type of membranes. These electrodes are called specific ion electrodes and are used conveniently for determining the activity of a given ion using a sensitive pH meter.

EXAMPLE 15.7 The e.m.f. of the cell

$$\text{Pt} \mid \text{H}_2(740\text{ torr}) \mid \text{Solution of unknown } p\text{H} \parallel 1\,\text{M KCl}, \text{Hg}_2\text{Cl}_2(\text{s}) \mid \text{Hg(l)} \mid \text{Pt}$$

at 298 K is 0.480. The electrode potential of the reference calomel electrode is 0.280 V. Calculate the pH of the solution.

Solution The e.m.f. of the cell is

$$E_{\text{cell}} = E_{\text{reference}} - E_{\text{hydrogen}}$$

The electrode potential for the hydrogen electrode,

$$\text{H}^+ + \text{e}^- \rightleftharpoons \tfrac{1}{2}\text{H}_2(\text{g})$$

$$E = -\frac{RT}{F} \ln \frac{[f_{(\text{H}_2)}]^{\frac{1}{2}}}{a_{(\text{H}^+)}} = \frac{2.303\,RT}{2F} \log p_{(\text{H}_2)} - \frac{2.303\,RT}{F}\,p\text{H}$$

$$p_{(\text{H}_2)} = \frac{740}{760} = 0.974\text{ atm}$$

$$\text{At 298 K, } E = -\frac{0.0591}{2} \log 0.974 - 0.0591\,p\text{H}$$

Thus, $E_{\text{cell}} = E_{\text{reference}} - E_{\text{hydrogen}}$

$$0.480 = 0.280 + \frac{0.0591}{2} \log 0.974 + 0.0591\,p\text{H}$$

or $0.480 = 0.280 - 0.0003 + 0.0591\,p\text{H}$

$$0.0591\,p\text{H} = 0.2003$$

$$\text{or } p\text{H} = \frac{0.2003}{0.0591} = 3.39$$

EXAMPLE 15.8 To calculate the pH of a given solution A, the quinhydrone electrode was coupled with a saturated calomel electrode as

$$\text{Pt} \mid \text{Hg(l)}, \text{Hg}_2\text{Cl}_2(\text{s}); \text{KCl (sat. soln)} \parallel \text{Solution } A; \text{Q}, \text{QH}_2 \mid \text{Pt}$$

The e.m.f. of the cell was found to be 0.123 V at 298 K. Calculate the pH of the solution. $E_{\text{calomel}} = 0.2415$ V and $E^\circ(\text{H}^+, \text{Q}, \text{QH}_2) = 0.6996$ V.

Solution The e.m.f. of the cell,

$$E_{\text{cell}} = E_{\text{quinhydrone}} - E_{\text{calomel}}$$

$E_{\text{quinhydrone}}$ can be calculated from the reaction,

$$\text{Q} + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{QH}_2$$

$$E_{\text{quinhydrone}} = \overset{\circ}{E}_{\text{quinhydrone}} - \frac{RT}{2F} \ln \frac{1}{[a_{(\text{H}^+)}]^2}$$

$$= 0.6996 - \frac{2.303\ RT}{F}\ p\text{H}$$

At 298 K,

$E_{\text{quinhydrone}} = 0.6996 - 0.0591\ p\text{H}$
and $E_{\text{calomel}} = 0.2415$ V
Now, $E_{\text{cell}} = E_{\text{quinhydrone}} - E_{\text{calomel}}$
$0.123 = 0.6996 - 0.0591\ p\text{H} - 0.2415$

$$p\text{H} = \frac{0.3351}{0.0591} = 5.67$$

15.10 SOLUBILITY PRODUCT FROM E.M.F. DATA

In a saturated solution of a sparingly soluble salt such as AgCl, equilibrium is represented as

$$\text{AgCl (s)} \rightleftharpoons \text{Ag}^+ \text{ (aq)} + \text{Cl}^- \text{ (aq)}$$

The product of the activities of Ag^+ and Cl^- ions is the solubility product

$$K_{sp} = [a_{(Ag^+)}] \times [a_{(Cl^-)}]$$

Since the solubility product is the equilibrium constant, it must be related to the e.m.f. of the selected cell having an overall reaction as above. For example, for determining the solubility product of AgCl, the cell is

$$\text{Ag} \mid \text{Ag}^+ \text{Cl}^- \text{(sat), Ag Cl(s)} \mid \text{Ag}$$

At anode, $Ag(s) = Ag^+ + e^-$
At cathode, $AgCl(s) + e^- = Ag + Cl^-$
So that the overall reaction is

$$\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$$

and $$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln [a_{(Ag^+)}][a_{(Cl^-)}]$$

$$= \frac{RT}{nF} \ln K_{sp}$$

Knowing the value of E°, K_{sp} can be calculated.

EXAMPLE 15.9 Calculate K_{sp} of AgCl by forming a suitable cell, given that $E^\circ(\text{AgCl, Ag, Cl}^-) = 0.2224$ V and $E^\circ(\text{Ag}^+, \text{Ag}) = 0.7991$ V

Solution

The cell can be represented as
$\text{Ag} \mid \text{Ag}^+ \text{Cl}^- \text{(sat)} \mid \text{AgCl(s)} \mid \text{Ag}$
At the left electrode,
$Ag(s) \rightleftharpoons Ag^+ + e^-$
At the right electrode,
$AgCl(s) + e^- \rightleftharpoons Ag + Cl^-$

Overall reaction:

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

$$\overset{\circ}{E}_{cell} = E_R - E_L$$
$$= 0.2224 - 0.7990$$
$$= -0.5766 \text{ V}$$

Now, $$E^\circ = \frac{RT}{nF} \ln K_{sp}$$

or $$\ln K_{sp} = \frac{nFE^\circ}{RT}$$

$$\log K_{sp} = \frac{(1)\times(96500 \text{ C mol}^{-1})\times(-0.5766 \text{ V})}{2.303\times(8.314 \text{ J K}^{-1} \text{ mol}^{-1})\times(298 \text{ K})}$$
$$= -9.75$$
$$K_{sp} = 5.6\times 10^{-9}$$

15.11 DETERMINATION OF ACTIVITY COEFFICIENTS FROM E.M.F.

E.m.f. measurements provide the most convenient method of determining activity coefficients of ions. Consider a simple cell,

$$Pt \mid H_2(1 \text{ atm}) \mid HCl(m) \parallel AgCl(s) \mid Ag$$

The overall cell reaction is

$$\tfrac{1}{2}H_2(g) + AgCl(s) \longrightarrow Ag(s) + H^+ + Cl^-$$

$$E_{cell} = E^\circ - \frac{2.303 \; RT}{nF} \log \frac{a_{(H^+)} \; a_{(Cl^-)}}{[f_{(H_2)}]^{\frac{1}{2}}}$$

The activities of solid Ag and AgCl are taken constant and the fugacity of hydrogen at 1 atm is also unity, so that

$$E = E^\circ - 0.0591 \log a_{(H^+)} \; a_{(Cl^-)}$$

Now $\quad a_{(H^+)} = \gamma_+ \, m_{(H^+)}; \qquad a_{(Cl^-)} = \gamma_- \, m_{(Cl^-)}$

For $\quad HCl, m_+ = m_- = m$, so that

$$E = E^\circ - 0.0591 \log m^2 - 0.0591 \log \gamma_+ \gamma_-$$

For each ion, the activity coefficient $\gamma_+ \gamma_- = \gamma_\pm^2$

where $\gamma_\pm$ is called the mean activity coefficient.

$$E = E^\circ - 2\times 0.0591 \log m - 0.0591 \log \gamma_\pm^2$$

or $$E = E^\circ - 0.1182 \log m - 0.1182 \log \gamma_\pm.$$

Thus, knowing the value of E at a particular concentration m, and E°, the mean activity coefficient can be calculated.

EXAMPLE 15.10 For the cell at 298 K,

$$Pt \mid H_2 \text{ (1 atm) } HCl(m) \parallel AgCl(s) \mid Ag$$

the e.m.f. is 0.450 V when m is equal to 0.0134 mol dm^{-3}. Calculate the mean activity coefficient. ($E^\circ = 0.2224$ V)

Solution For the cell, the cell reaction is

$$\tfrac{1}{2} H_2(g) + AgCl(s) \rightleftharpoons Ag(s) + H^+ + Cl^-$$

$$E = E^\circ - \frac{2.303RT}{nF} \log \; a_{(H^+)} \, a_{(Cl^-)}$$

$$= E^\circ - 0.0591 \log m^2 - 0.0591 \log \gamma_\pm^2$$

$$= E^\circ - 0.1182 \log m - 0.1182 \log \gamma_\pm$$

$$E = 0.45 \text{ V}, E^\circ = 0.2224 \text{ V}, m = 0.0134$$

$$\therefore \; 0.1182 \log \gamma_\pm = E^\circ - 0.1182 \log m - E$$

$$= 0.2224 - 0.1182 \log (0.0134) - 0.450$$

$$= 0.2224 + 0.2214 - 0.450$$

$$= -0.0062$$

$$\log \gamma_\pm = -0.052$$

$$\therefore \quad \gamma_\pm = 0.887$$

15.12 CONCENTRATION CELLS

Electrical energy can also be obtained by the concentration difference of the solutions in which the electrodes are dipping. These cells are called concentration cells. In these cells, the free energies of solutions are different at two concentrations, and electrical energy arises from the transfer of substance from the solution of higher activity around one electrode (higher energy) to that of lower activity around the other electrode (lower energy). For example, in the case of a cell

$$\text{Zn} \mid \text{Zn}^{2+} (a_1) \parallel \text{Zn}^{2+} (a_2) \mid \text{Zn}$$

e.m.f. may be expressed as

$$E = -\frac{RT}{nF} \ln \frac{a_2}{a_1}$$

For e.m.f. to be positive, $a_1 > a_2$ so that the reaction proceeds in the direction indicated.

However, in case of gas electrodes such as

$$\text{Pt} \mid H_2 (p_1 \text{ atm}) \mid \text{HCl} \mid H_2 (p_2 \text{ atm}) \mid \text{Pt}$$

assuming that the behaviour of hydrogen is nearly ideal, e.m.f. may be written as

$$E = -\frac{RT}{nF} \ln \frac{p_2}{p_1}$$

15.13 JUNCTION POTENTIAL

A liquid junction between the solutions in a cell gives rise to a junction potential. The e.m.f. of the cell will depend on the transference numbers of the ions. Such cells are called concentration cells with transference. The e.m.f. of the cell will be equal to $E_{cell} + E_j$ where E_{cell} is the potential of the cell that would be observed in the absence of junction potential and E_j is the junction potential. E_l can be calculated as $E_j = E - (E_R - E_L)$.

Example 15.11 Calculate the e.m.f. of the cell at 25°C

$$\text{Pt} \mid H_2\ (700\ \text{torr}) \mid \text{HCl} \parallel H_2\ (420\ \text{torr}) \mid \text{Pt}$$

assuming that hydrogen behaves as an ideal gas

Solution The overall cell reaction is

$$H_2\ (700\ \text{torr}) = H_2\ (420\ \text{torr})$$

$$E = -\frac{RT}{2.303\,nF}\log\frac{420/760}{700/760}$$

$$= -\frac{0.0591}{2}\log\frac{420}{700}$$

$$= 6.56\times10^{-3}\ \text{V} = 6.56\ \text{mV}$$

Example 15.12 The potential difference between hydrogen electrodes in the cell

$$\text{Pt} \mid H_2\ (760\ \text{torr}),\ H^+\ (m_1=0.01) \parallel H^+\ (m_2=0.1) \mid H_2\ (760\ \text{torr}) \mid \text{Pt}$$

is 0.0558 V at 298 K. The activity coefficient of a 0.01 m HCl solution is 0.90, calculate the activity coefficient of an 0.1 m HCl solution.

Solution The potential difference between two hydrogen electrodes is

$$E = \frac{RT}{nF}\ln\frac{[a_{(H^+)}]_2}{[a_{(H^+)}]_1}$$

$$E = \frac{0.0591}{n}\log\frac{[a_{(H^+)}]_2}{[a_{(H^+)}]_1}$$

$$n = 1,\ [a_{(H^+)}]_2 = m_2\gamma_2 = 0.1\,\gamma_2 \text{ and } [a_{(H^+)}]_1 = m_1\gamma_1 = 0.01\times0.9$$

and $E = 0.0558$ V

$$0.0558 = \frac{0.0591}{1}\log\frac{0.1\,\gamma_2}{0.01\times0.9}$$

or

$$\log\frac{0.1\,\gamma_2}{0.01\times0.9} = \frac{0.0558}{0.0591} = 0.944$$

$$\frac{0.1\,\gamma_2}{0.01\times0.9} = 8.79$$

$$\therefore\quad \gamma_2 = \frac{8.79\times0.01\times0.9}{0.1}$$

$$= 0.79$$

15.14 ELECTRODE POLARIZATION

In case of cells functioning under reversible conditions, either there is no flow of current or only infinitesimally small currents flow through the cell. In such cases, under equilibrium state, the discharge of ions and their reformation occurs at the same rate. However, under irreversible conditions, an appreciable amount of current flows. Due to the passage of current, the concentration of the reactants and products around the electrode is different from its bulk concentration. This naturally changes its potential from the value under reversible conditions. This phenomenon of disturbance of equilibrium due to flow of current is called *electrolytic polarization* and the disturbed electrode is called *polarized*. Polarization is due to the slowness of one or more processes occurring at the electrode during the discharge or formation of ions. The nature of the slow process determines the type of polarization.

Concentration Polarization

This type of polarization is due to the change in concentration in the vicinity of the electrode. For example, when a metal is dipped into a solution of its own ions M^{z+} (activity $= a$), the reversible electrode potential of the electrode is

$$E = E^\circ - \frac{RT}{zF} \ln a$$

However, when an external e.m.f. is applied in such a way that the metal electrode is made the cathode, the M^{Z+} ion will start discharging on the electrode. The resulting concentration a' of the ion around the electrode will not be equal to a. Obviously, the potential given by the relation

$$E' = E^\circ - \frac{RT}{zF} \ln a'$$

will be higher than the reversible potential (E) of the electrode dipping into a solution of activity a. This change in potential of the electrode from its reversible value, due to change in the concentration of ions in its immediate neighbourhood, is called concentration polarization.

Over Voltage

In case of cells where evolution of gases occurs, it has been observed that, under irreversible conditions, the potential required is larger than the reversible potential. This difference between the potential of the electrode when gas evolution is actually observed and the theoretical reversible value for the same solution is called *over voltage*.

Over voltage varies with the nature of the metal and the solution in which it is dipped. This indicates that some step involved in the process of evolution of gas is slow.

15.15 THE DROPPING MERCURY ELECTRODE (POLAROGRAPHY)

Polarography is an important technique these days. In this, the cathode is a dropping mercury electrode, in which a mercury drop grows steadily, at the tip of a capillary dipping in the solution, and falls, keeping the cathode surface fresh. The anode is either a mercury pool or a calomel electrode. The polarographic cell is a small glass vessel fitted with a dropping mercury cathode. Variable voltage is applied across the cell and the current passing through it is measured. The current versus potential curve is called a *polarogram.* Discharge of each ion is represented by a single step, called a polarographic wave, in the polarogram. Polarography can be used to determine the number of electrons involved in the reduction process and is used to determine stability constants of complexes. These days, different variation of the parent technique, e.g. A.C. polarography, pulse polarography, etc. are available.

MISCELLANEOUS EXAMPLES

EXAMPLE 15.13 The e.m.f. of two cells at 298K are

$\mathrm{Pt} \mid \mathrm{H_2(1\ atm)},\ \mathrm{HCl}(a = 1) \parallel \mathrm{Cl_2(1\ atm)} \mid \mathrm{Pt};\ E^\circ = 1.3595\ \mathrm{V}$

and $\mathrm{Pt} \mid \mathrm{Cl_2(1\ atm)},\ \mathrm{HCl}(a = 1) \parallel \mathrm{AgCl(s)} \mid \mathrm{Ag};\ E^\circ = -1.137\ \mathrm{V}$

Predict the e.m.f. of the cell

$\mathrm{Ag} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl}(a = 1) \parallel \mathrm{Cl_2(1\ atm)} \mid \mathrm{Pt}$

Solution For the cell

$\mathrm{Pt} \mid \mathrm{H_2(1\ atm)},\ \mathrm{HCl}(a = 1) \parallel \mathrm{Cl_2(1\ atm)} \mid \mathrm{Pt}$

$$E_{\text{cell}} = E_R - E_L$$
$$= E^\circ(\mathrm{Cl_2, Cl^-}) - E^\circ(\mathrm{H^+, H_2})$$
$$E_{\text{cell}} = 1.3595\ \mathrm{V},\ E^\circ(\mathrm{H^+, H_2}) = 0 \text{ (by convention)}$$
$$1.3595\ \mathrm{V} = E^\circ(\mathrm{Cl_2, Cl^-})$$
$$E^\circ(\mathrm{Cl_2, Cl^-}) = 1.3595\ \mathrm{V}$$

For the cell

$\mathrm{Pt} \mid \mathrm{Cl_2(1\ atm)},\ \mathrm{HCl}\ (a = 1) \parallel \mathrm{AgCl(s)} \mid \mathrm{Ag}$

$$E_{\text{cell}} = E^\circ(\mathrm{Ag^+, Ag}) - E^\circ(\mathrm{Cl_2, Cl^-})$$
$$E_{\text{cell}} = -1.1370\ \mathrm{V},\ E^\circ(\mathrm{Cl_2, Cl^-}) = 1.3595\ \mathrm{V}$$

so that
$$-1.1370\ \mathrm{V} = E^\circ_{(\mathrm{Ag^+, Ag})} - 1.3595\ \mathrm{V}$$
$$E^\circ_{(\mathrm{Ag^+, Ag})} = 1.3595 - 1.1370 = 0.2225\ \mathrm{V}$$

For the cell

$\mathrm{Ag} \mid \mathrm{AgCl(s)} \mid \mathrm{HCl}(a = 1) \parallel \mathrm{Cl_2(1\ atm)} \mid \mathrm{Pt}$

$$E^\circ_{\text{cell}} = E^\circ_{(\mathrm{Cl_2, Cl^-})} - E^\circ_{(\mathrm{Ag^+, Ag})}$$
$$= 1.3595 - 0.2225 = 1.1370\ \mathrm{V}$$

EXAMPLE 15.14 The free energy of formation of liquid water at 298 K is − 237.2 kJ mol, and the free energy of ionization of liquid water to hydrogen and hydroxyl ions is 79.7 kJ/mol.

(a) What will be the reversible e.m.f. of the cell

$\mathrm{H_2(1\ atm)} \mid \mathrm{H^+} \parallel \mathrm{OH^-} \mid \mathrm{O_2(1\ atm)}$?

(b) If ΔH of the cell reaction is $-$ 172 kJ/mol, what will be (i) the temperature coefficient of the cell at 298 ? (ii) ΔS for the reaction ?

Solution

(a) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta G = -\ 237.2\ \text{kJ}$ (i)

$H_2O(l) \longrightarrow H^+ + OH^- \qquad \Delta G = 79.7\ \text{kJ}$ (ii)

The cell is

$H_2(1\ \text{atm})\ |\ H^+\ \|\ OH^-\ |\ O_2\ (1\ \text{atm})$

The reaction at the left electrode $\quad H_2 \rightleftharpoons 2H^+ + 2e^-$

The reaction at the right electrode $\quad H_2O + \frac{1}{2}O_2 \rightleftharpoons 2OH^-$

The cell reaction $\quad H_2O + \frac{1}{2}O_2 + H_2 \longrightarrow 2H^+ + 2OH^-$ (iii)

The cell reaction can be obtained by multiplying Eq. (ii) by 2 and subtracting from Eq. (i).

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \qquad \Delta G = -\ 237.2\ \text{kJ}$

$2H_2O(l) \longrightarrow 2H^+ + 2OH^- \qquad \Delta G = 159.4\ \text{kJ}$

$H_2O(l) + \frac{1}{2}O_2(g) + H_2(g) \longrightarrow 2H^+ + 2OH^-\ \Delta G = -\ 77.8\ \text{kJ}$

Now $\Delta G = -\ nFE$

$$\text{or} \qquad E = -\frac{\Delta G}{nF}$$

$n = 2,\ F = 96500\ \text{C}$

$$E = -\frac{-\ 77.8 \times 10^3\text{J}}{2 \times 96500\text{C}} = 0.403\ \text{J C}^{-1} = 0.403\ \text{V}$$

(b) $\Delta G = \Delta H - T\Delta S$

$\Delta G = -\ 77.8\ \text{kJ},\ \Delta H = -\ 172.0\ \text{kJ}$

$$T\Delta S = \Delta H - \Delta G$$

$$= -\ 172.0 - 77.8 = -\ 94.2\ \text{kJ}$$

$$\Delta S = -\frac{94.2 \times 10^3\text{J}}{298\ \text{K}} = -\ 316.1\ \text{J K}^{-1}$$

$$\text{Now, } \Delta S = nF\left(\frac{\partial E}{\partial T}\right)_p$$

$$\text{or } \left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta S}{nF}$$

$$= \frac{-\ 316.1\ \text{J K}^{-1}}{2 \times 96500\ \text{C}}$$

$$= -\ 0.00164\ \text{J C}^{-1}\ \text{K}^{-1}$$

$$= -\ 0.00164\ \text{V K}^{-1}$$

EXAMPLE 15.15 The reaction in a fuel cell is

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

$$E^\circ(O_2, H^+, H_2O) = 1.229\ \text{V}$$

(a) Calculate the equilibrium constant for the cell reaction.

(b) What is the maximum e.m.f. obtainable from the above cell if both hydrogen and oxygen are at 1 atm pressure ?

(c) What is the maximum amount of electrical work available per mole of hydrogen ?

(d) How many amperes per hour electricity would be supplied by such a cell containing ten moles of hydrogen ?

Solution

(a) Left electrode : $H_2 \longrightarrow 2H^+ + 2e^-$
Right electrode : $2H^+ + \frac{1}{2}O_2 + 2e^- \rightleftharpoons H_2O$
Cell reaction : $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$
$E_{cell} = E_R - E_L = 1.229 - 0 = 1.229$ V

(b) The maximum e.m.f. obtainable from the cell = 1.229 V

(c) Now, $\Delta G^\circ = -nFE^\circ$

$$= -(2) \times 96500 \text{ C mol}^{-1} \times 1.229 \text{ V}$$
$$= -237.2 \text{ kJ}$$

Maximum amount of electrical work available = 237.2 kJ per mole of hydrogen

(d) Amount of electricity produced for one mole of hydrogen

$$= 2 \times 96500 \text{ C}$$

Amount of electricity produced for ten moles of hydrogen

$$= 2 \times 96500 \times 10 \text{ C}$$
$$= 193 \times 10^5 \text{C}$$

$$\text{Electricity supplied per hour} = \frac{193 \times 10^5}{60 \times 60} = 5.36 \times 10^3 \text{Ch}^{-1}$$

QUESTIONS

Numerical Problems

15.1 Write the equations for left- and right-hand electrode reactions and the overall cell reactions for the following:
(a) Pt | H_2, H^+ ‖ Cu^{2+} | Cu
(b) Zn | Zn^{2+} ‖ Cl^-, Hg_2Cl_2(s) | Hg(l)
(c) Ag | Ag^+Br^- ‖ AgBr(s) | Ag
(d) Cr | $CrCl_3$(aq) ‖ KCl(aq) | Hg_2Cl_2(s) | Hg(l)

15.2 (SI units) A zinc–zinc ion electrode potential is measured by coupling with a saturated calomel electrode at 298 K. The zinc electrode is negative and the observed e.m.f. is 1.0045 V. What is the cell reaction and the electrode potential of the zinc–zinc ion electrode, given that the electrode potential of the calomel electrode is 0.2415 V ?

15.3 Find the standard e.m.f. of the cells :
(a) Cu | Cu^{2+} $(a = 1)$ ‖ Cl^- $(a = 1)$, Cl_2(1 atm) | Pt
(b) Zn | Zn^{2+} $(a = 1)$ ‖ Cd^{2+} $(a = 1)$ | Cd
(c) I_2 | I^- $(a = 1)$ ‖ Ce^{4+} $(a = 1)$, Ce^{3+} $(a = 1)$ | Pt
The standard electrode potentials are $E^\circ(Cu^{2+}, Cu) = 0.337$ V,

$E^\circ(Cl_2, Cl^-) = 1.3595$ V, $E^\circ(Zn^{2+}, Zn) = -0.763$ V, $E^\circ(Cd^{2+}, Cd) = -0.403$ V, $E^\circ(Ce^{4+}, Ce^{3+}) = 1.440$ V, $E^\circ(I_2, I^-) = 0.536$.

15.4 The standard electrode potentials $E^\circ(I_2, I^-)$ and $E^\circ(Cl_2, Cl^-)$, are 0.536 and 1.360 V, respectively. Will iodine liberate chlorine from a solution of chloride ions (unit activity) ?

15.5 Predict whether the following reactions will occur spontaneously or not:

(a) $2Cu^+(a = 1) \longrightarrow Cu + Cu^{2+}(a = 1)$
$E^\circ(Cu^+, Cu) = 0.521$ V, $E^\circ(Cu^{2+}, Cu) = 0.337$

(b) $AgCl(s) + I^-(a = 1) \longrightarrow AgI(s) + Cl^-(a = 1)$
$E^\circ(AgCl, Ag) = 0.2223$ V, $E^\circ(AgI, Ag) = -0.151$ V

(c) $Mn^{2+} + 4H_2O + Fe^{3+} \longrightarrow MnO_4^- + 5Fe^{2+} + 8H^+$

$E^\circ(Fe^{3+}, Fe^{2+}) = 0.771$ V; $E^\circ(MnO_4^-, H^+ Mn^{2+}) = 1.51$ V

15.6 Will Fe^{2+} be oxidized to Fe^{3+} by (a) acidified permanganate ions (b) chlorine ?

Given that: $E^\circ(Fe^{3+}, Fe^{2+}) = 0.771$ V, $E^\circ(MnO_4^-, H^+, Mn^{2+}) = 1.51$ V, and $E^\circ(Cl_2, Cl^-) = 1.360$ V.

15.7 (SI units) Calculate the e.m.f. of the following cells at 298 K:

(a) $Zn \mid Zn^{2+}(a = 0.205) \parallel Fe^{2+}(a = 0.125) \mid Fe$
$E^\circ(Zn^{2+}, Zn) = -0.763$ V, $E^\circ(Fe^{2+}, Fe) = -0.440$ V

(b) $Pb \mid Pb^{2+}(a = 0.0018) \parallel Fe^{2+}(a = 0.2), Fe^{3+}(a = 0.15) \mid Pt$
$E^\circ(Pb^{2+}, Pb) = -0.126$ V, $E^\circ(Fe^{3+}, Fe^{2+}) = 0.771$ V

15.8 The e.m.f. for the cell reaction
$2\,Co + 2Ni^{2+} = 2Co^{2+} + Ni$
is 0.003 V. What will be the increase or decrease in cell potential if the concentration ratio $a_{(Co^{2+})}/a_{(Ni^{2+})}$ is changed by a factor of (a) 10 (b) 0.1 ?

15.9 Calculate the standard e.m.f. and standard free energy change for the cell in which the reaction
$Fe^{2+} + \frac{1}{2}Br_2(l) = Br^- + Fe^{3+}$
takes place. $E^\circ(Fe^{3+}, Fe^{2+}) = 0.771$ V, $E^\circ(Br_2, Br^-) = 1.065$

15.10 Write the cell reactions and calculate the standard free energy changes for the following cells:

(a) $Pt \mid Tl^+ (a = 1), Tl^{3+}(a = 1) \parallel Cl^-(a = 1), Hg_2Cl_2(s) \mid Hg$
$E^\circ(Tl^{3+}, Tl^+) = -1.25$ V, $E^\circ(Hg_2Cl_2, Cl^-) = 0.2676$ V

(b) $Pt \mid H_2(1\ atm), H^+(a = 1) \parallel Cl^-(a = 1), Cl_2(1\ atm) \mid Pt$
$E^\circ(Cl_2, Cl^-) = 1.350$ V

15.11 Calculate the e.m.f. of the cell corresponding to the cell reaction:
$\frac{1}{2}H_2(g)(1\ atm) + AgCl(s) \rightleftharpoons Ag(s) + H^+(a = 0.1) + Cl^-(a = 0.1)$
The standard free energy change for the above cell reaction at 298 K is -21.45 kJ.

15.12 The standard e.m.f. of the cell
$Pb(s) \mid PbCl_2, Cl^-(a = 1) \parallel Cl^-(a = 1), Hg_2Cl_2 \mid Hg(l)$
at 298 K is 0.536 V. The temperature coefficient of the e.m.f. at constant pressure has been found to be 0.145 mV K^{-1}. Calculate ΔG°, ΔS° and ΔH° for the cell reaction.

15.13 Calculate ΔG° and the equilibrium constant for the cell reaction
$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$
given that $E^\circ(Cl_2, Cl^-) = 1.36$ V, $E^\circ(I_2, I^-) = 0.536$ V.

15.14 The equilibrium constant for the reaction
$Ce^{4+} + Fe^{2+} \rightleftharpoons Ce^{3+} + Fe^{3+}$

at 298 K is 1.6×10^{-14}. Calculate E°_{cell} and ΔG° for the above reaction.

15.15 The e.m.f. of the cell

$\mathrm{Pt} \mid H_2(1\ \text{atm}), \mathrm{HCl} \parallel \mathrm{AgCl} \mid \mathrm{Ag}$

is 0.380 V at 98 K. What is the *p*H of the solution $\left(E^\circ_{(\mathrm{AgCl, Cl^-})} = 0.2223\ \mathrm{V}\right)$?

15.16 Calculate K_{sp} of TlBr at 25°C by forming a suitable cell, given that $E^\circ_{(\mathrm{TlBr,\ Tl})} = -\,0.658\ \mathrm{V}$, $E^\circ_{(\mathrm{Tl^+,\ Tl})} = -\,0.336\ \mathrm{V}$.

15.17 The solubility of AgI at 298 K is 9.2×10^{-9} mol kg^{-1}. Calculate the e.m.f. of the cell

$\mathrm{Ag} \mid \mathrm{AgI(aq)} \parallel \mathrm{AgI} \mid \mathrm{Ag}$

15.18 Calculate the equilibrium constant for the reaction:

$$\mathrm{Ag} + \mathrm{Fe^{3+}} \rightleftharpoons \mathrm{Ag^+} + \mathrm{Fe^{2+}}$$

The standard electrode potentials of the electrodes

$$\mathrm{Ag^+} \mid \mathrm{Ag} \text{ and } \mathrm{Fe^{3+}, Fe^{2+}} \mid \mathrm{Pt}$$

are 0.7991 V and 0.771 V respectively.

15.19 The e.m.f. of the cell consisting of oxidation half reaction

$$\mathrm{Cr^{2+}}(a = 1) \longrightarrow \mathrm{Cr^{3+}}(a = 0.1) + e^-$$

and reduction half reaction $\mathrm{Fe^{3+}}(a = 0.5) + e^- \rightleftharpoons \mathrm{Fe^{2+}}\ (a = 1)$ at 298 K is 1.216 V. Calculate

(a) the standard e.m.f. of the cell
(b) the standard free energy change for the cell reaction

15.20 For the cell

$\mathrm{Pt} \mid \mathrm{Hg(l)} \mid \mathrm{KCl\ (1M)}\ \mathrm{Hg_2Cl_2(s)} \parallel \mathrm{H^+}[a_{(\mathrm{H^+})}]Q, QH_2 \mid \mathrm{Pt}$

Calculate the e.m.f. when *p*H = 4 at 298 K.

$(E^\circ_{\text{calomel}} = 0.280\ \mathrm{V}$ and $E^\circ_{(Q,\ QH_2\ \mathrm{H^+} \mid \mathrm{Pt})} = 0.6996\ \mathrm{V})$

QUIZ QUESTIONS

Type A: Multiple Choice

15.21 In the cell reaction

$$\mathrm{Cu(s)} + 2\mathrm{Ag^+(aq)} \longrightarrow \mathrm{Cu^{2+}(aq)} + 2\mathrm{Ag(s)}$$

the reduction half reaction is

(a) $\mathrm{Cu(s)} - 2e \rightarrow \mathrm{Cu^{2+}(aq)}$
(b) $\mathrm{Cu^{2+}(aq)} + 2e \rightarrow \mathrm{Cu(s)}$
(c) $2\ \mathrm{Ag(s)} \rightarrow 2\ \mathrm{Ag^+(aq)} + 2e$
(d) $2\ \mathrm{Ag^+(aq)} + 2e \rightarrow 2\ \mathrm{Ag(s)}$

15.22 Free energy change (ΔG) is related to the e.m.f. of a cell (E) as

(a) $\Delta G = -\dfrac{RT}{nF} \ln E$
(b) $\Delta G = -\,nFE$
(c) $E = -\,nF\,\Delta G$
(d) $\Delta G = -\dfrac{nFE}{RT}$

15.23 According to the latest convention, the e.m.f. of a cell may be expressed in terms of the reduction potentials RHS electrode (E_R) and LHS electrode (E_L) as

(a) $E_{\text{cell}} = E_L - E_R$
(b) $E_{\text{cell}} = E_R - E_L$
(c) $E_{\text{cell}} = E_R + E_L$
(d) $E_{\text{cell}} = E_R / E_L$

15.24 Which of the following statements is not correct regarding galvanic cells?

(a) Oxidation occurs at the anode

(b) Ions carry current inside the cell

(c) Electrons flow around the external circuit, from cathode to anode

(d) When the e.m.f. of the cell is positive cell reaction is spontaneous.

15.25 The electrode $Pt/Fe^{2+}(C_1)$, $Fe^{3+}(C_2)$ belongs to the type

(a) gas electrodes

(b) inert metal electrodes

(c) amalgam electrodes

(d) metal–metal insoluble salt electrodes

15.26 The entropy change (ΔS) for a cell reaction is given by

(a) $nF\left(\frac{\partial E}{\partial T}\right)_p$

(b) $nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right]$

(c) $-nF\left(\frac{\partial E}{\partial T}\right)_p$

(d) $-\frac{RT}{nF}\ln\left(\frac{\partial E}{\partial T}\right)_p$

15.27 The equilibrium constant (K) for a cell reaction can be calculated from the e.m.f. of the cell (E°) by the relation

(a) $K = \frac{2.303\,RT}{nF}\log E^\circ$

(b) $\log K = \frac{nFE^\circ}{2.303\,RT}$

(c) $K = \frac{2.303\,RT}{nFE^\circ}$

(d) $K = \frac{2.303\,nF}{RT}\log E^\circ$

15.28 The Nernst equation for the e.m.f. of the cell for the

$$aA + bB \rightarrow cC + dD$$

is

(a) $E = E^\circ + \frac{RT}{nF}\ln\frac{(a_C)^c\,(a_D)^d}{(a_A)^a\,(a_B)^b}$

(b) $E + E^\circ = \frac{RT}{nF}\ln\frac{(a_C)^c\,(a_D)^d}{(a_A)^a\,(a_B)^b}$

(c) $E = E^\circ - \frac{nRT}{F}\ln\frac{(a_C)^c\,(a_D)^d}{(a_A)^a\,(a_B)^b}$

(d) $E = E^\circ - \frac{RT}{nF}\ln\frac{(a_C)^c\,(a_B)^b}{(a_A)^a\,(a_B)^b}$

15.29 If $2.303RT/F = 0.059$ and the activities of the solids are constant, then e.m.f. of the cell

$$Zn \mid Zn^{2+}\,(a_1) \parallel Cu^{2+}\,(a_2) \mid Cu$$

is

(a) $E = E^\circ - 0.059 \log\frac{a_2}{a_1}$

(b) $E = E^\circ + 0.059 \log\frac{a_1}{a_2}$

(c) $E = E^\circ - \frac{0.059}{2}\log\frac{a_1}{a_2}$

(d) $E = E^\circ + \frac{0.059}{2} \log \frac{a_2}{a_1}$

15.30 A half cell reaction is one that
(a) occurs at one electrode
(b) goes only half way to completion
(c) involves a half mole of the concentration of the solution
(d) always oxidises

15.31 The e.m.f. of a concentration cell with transference of cations from the solution of higher activity (a_1) to that lower activity (a_2) is given by

(a) $E = -\frac{RT}{nF} \ln \frac{a_2}{a_1}$

(b) $E = -\frac{RT}{nF} \log \frac{a_1}{a_2}$

(c) $E = -\frac{2.303RT}{nF} \log \frac{a_1}{a_2}$

(d) $E = \frac{-RT}{nF} \ln \frac{a_1}{a_2}$

15.32 If $2.303RT/F = 0.059$ and the standard potential of the reference electrode is X V, the pH of the solution can be calculated from the e.m.f. (E) of the cell. Reference electrode $\| H^+[a_{(H^+)}], H_2$ (1 atm) | Pt using equation

(a) $pH = \frac{E + X}{0.059}$

(b) $\frac{0.059 - X}{E}$

(c) $pH = -\frac{E + X}{0.059}$

(d) $0.059 \times \frac{E}{X}$

15.33 For the galvanic cell

$$Zn \mid Zn^{2+} [a_{(Zn^{2+})}] \parallel Cu^{2+} [a_{(Cu^{2+})}] \mid Cu$$

where $a_{(Zn^{2+})}$ and $a_{(Cu^{2+})}$ are the activities of the Zn^{2+} and Cu^{2+} ions. The e.m.f. of the cell

(a) increases with increase of $a_{(Zn^{2+})}$ when $a_{(Cu^{2+})}$ = constant
(b) increases with decrease of $a_{(Cu^{2+})}$ when $a_{(Zn^{2+})}$ = constant
(c) increases when $a_{(Zn^{2+})}$ decreases and $a_{(Cu^{2+})}$ increases
(d) decreases when $a_{(Zn^{2+})}$ decreases and $a_{(Cu^{2+})}$ increases

15.34 Concentration polarization arises because of the
(a) different concentrations of solutions in the two half cells
(b) changes in the concentration of electrolyte around the electrode from bulk concentration
(c) reversible nature of the cell
(d) variation in temperature during measurements

15.35 In a standard Weston cell, the cathode is
(a) cadmium amalgam
(b) mercury
(c) platinum
(d) carbon

15.36 The electrode reaction for the electrode Ag, Ag_2O/H_2O, OH^- at the anode is

(a) $2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e^-$

(b) $Ag \rightarrow Ag^+ + e^-$

(c) $Ag_2O + H_2O + 2e^- \rightarrow Ag_2O + OH^-$

(d) $2Ag + H_2O \rightarrow Ag_2O + H_2$

15.37 The reduction electrode potential for the electrode Pt | Tl^{3+}, Tl^+ may be written as

(a) $E = E^\circ - \dfrac{RT}{F} \ln \dfrac{a_{(Tl^{3+})}}{a_{(Tl^+)}}$

(b) $E = E^\circ + \dfrac{RT}{2F} \ln \dfrac{a_{(Tl^+)}}{a_{(Tl^{3+})}}$

(c) $E = E^\circ - \dfrac{RT}{F} \log \dfrac{a_{(Tl^+)}}{a_{(Tl^{3+})}}$

(d) $E = E^\circ - \dfrac{RT}{2F} \ln \dfrac{a_{(Tl^+)}}{a_{(Tl^{3+})}}$

15.38 To calculate the solubility product of AgI, the following cell was constructed

Ag | Ag^+, I^- ‖ AgI(s) | Ag

If E° is the standard electrode potential, then K_{sp} is given as

(a) $\log K_{sp} = \dfrac{nFE^\circ}{2.303RT}$

(b) $K_{sp} = \dfrac{nF}{2.303RT} \log E^\circ$

(c) $\ln K_{sp} = \dfrac{nF}{E^\circ}$

(d) $\ln K_{sp} = nF\left[\left(\dfrac{\partial E^\circ}{\partial T}\right)_p - E^\circ\right]$

15.39 The cell reaction in the cell formed by coupling the two standard electrodes

Pt | H_2, H^+ ($E = 0$) and Ag | AgCl, Cl^-

($E = 0.2223$ V) is

(a) $\frac{1}{2} H_2$ (1 atm) + Ag^+ ($a = 1$) $\rightleftharpoons$ Ag(s) + H^+($a = 1$)

(b) $\frac{1}{2} H_2$ (1 atm) + AgCl(s) $\rightleftharpoons$ H^+ ($a = 1$) + Cl^-($a = 1$) + Ag^+($a = 1$)

(c) Ag(s) + H^+($a = 1$) + Cl^-($a = 1$) $\rightleftharpoons$ AgCl(s) + $\frac{1}{2} H_2$ (1 atm)

(d) $\frac{1}{2} H_2$ (1 atm) + AgCl(s) $\rightleftharpoons$ H^+ ($a = 1$) + Cl^- ($a = 1$) + Ag(s)

15.40 If the solubility of AgBr is x mol kg^{-1} at 25°C, the e.m.f. of the cell is given by

(a) $0.0591\, x$ (b) $0.0591 \log x^2$

(c) $0.0591 \log x$ (d) $0.0591/2 \log (2x)$

Type B: Multiple Choice (Numerical Problems)

15.41 The standard electrode potential of Zn | Zn^{2+} is -0.763 V. The e.m.f. of the cell represented by the cell reactions

Zn(s) + $2H^+$ ($a = 1$) $\rightleftharpoons$ Zn^{2+} ($a = 1$) + H_2 (1 atm) is

(a) 0.763 V (b) zero

(c) -0.763 V (d) cannot be calculated

15.42 The standard electrode potentials of Zn | Zn^{2+} and Cu | Cu^{2+} are -0.763 and 0.337 V, respectively. The standard e.m.f. of the cell

Zn | Zn^{2+} ($a = 1$) ‖ Cu^{2+} ($a = 1$) | Cu is

(a) 1.10 V (b) 0.426 V

(c) -1.10 V (d) zero

15.43 The e.m.f. of the cell Zn | Zn^{2+} (0.01) ‖ Fe^{2+} (0.001) | Fe

($\overset{\circ}{E}_{cell} = 0.323$ V) at 25°C is

(a) 0.352 V
(b) − 0.323 V
(c) 0.293 V
(d) 3.23 V

15.44 Given that E° (Zn^{2+}, Zn) = −0.763 V and E° (Cu^{2+}, Cu) = 0.337, the e.m.f. of the cell

Zn | Zn^{2+} ($a = 0.01$) ‖ Cu^{2+} ($a = 0.025$) | Cu

(a) $= -1.10 - \frac{0.059}{2} \log \frac{0.01}{0.25}$

(b) $= 1.10 + \frac{0.059}{2} \log \frac{0.25}{0.01}$

(c) $= 1.10 - \frac{0.059}{2} \log \frac{0.25}{0.01}$

(d) $= 1.10 - 0.059 \log \frac{0.01}{0.25}$

15.45 The e.m.f. of the concentration cell consisting of two zinc electrodes, one immersed in a solution of $a = 0.02$ and the other in a solution of $a = 0.2$ concentration of its ions at 25°C, will be

(a) 0.059 log 0.004
(b) 0.0295
(c) 0.059
(d) log 0.59

15.46 The e.m.f. of the concentration cell with transference is 0.048 V and the e.m.f. of the cell without liquid junction is 0.059 V. The liquid junction potential is

(a) − 0.011 V
(b) 0.107 V
(c) 0.011 V
(d) − 0.107 V

15.47 For an overall cell reaction of a fuel cell

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)$

at 400 K, ΔH and ΔS have been found to be − 251.6 kJ and −50 J K^{-1}, respectively. The e.m.f. of the cell is

(a) 1.2 V
(b) 2.4 V
(c) 1.4 V
(d) 2.8 V

15.48 For the cell reaction

$Hg_2Cl_2(s) + H_2\ (1\ atm) \longrightarrow 2Hg(l) + 2H^+\ (a = 1) + 2Cl^-\ (a = 1)$

$E^\circ = 0.268$ V and $\left(\frac{\partial E}{\partial T}\right)_p = -3.2 \times 10^{-4}$ V K^{-1}. The change in entropy of the cell reaction is

(a) − 61.76 J K^{-1}
(b) − 30.88 J K^{-1}
(c) 62.028 J K^{-1}
(d) −0.268 J K^{-1}

15.49 For a cell reaction

$Zn(s) + Mg^{2+}\ (a = 0.1) \rightleftharpoons Zn^{2+}\ (a = 1) + Mg$

the e.m.f. has been found to be 0.2312 V. The standard e.m.f. of the cell is

(a) 0.2903
(b) − 0.2312
(c) 0.0231
(d) 0.2670

15.50 For a cell reaction, the standard e.m.f. has been found to be 0.295 V at 298 K. The equilibrium constant is

(a) 29.5
(b) 10
(c) 1.0×10^{10}
(d) 0.1

Type C: True or False

15.51 According to cell conventions, oxidation occurs at the anode.

15.52 The potential for the same electrode, when acting as an anode, is of opposite sign to its potential when it acts as a cathode.

15.53 In a polarograph, the dropping mercury electrode acts as the anode.

15.54 Concentration polarization takes place in the case of galvanic cells functioning under irreversible conditions.

15.55 For *p*H determination, the quinhydrone electrode works satisfactorily only at high *p*H values.

15.56 A positive value for the e.m.f. of the cell indicates a spontaneous process in the given direction.

15.57 In case of reversible electrode processes, an appreciable amount of current flows through the cell.

15.58 The Nernst equation gives the relation between e.m.f. of the cell and free energy change.

15.59 In concentration cells, electrical energy arises from the transfer of a substance from a solution of higher activity to one of lower activity.

15.60 In a cell under irreversible conditions, the potential of an electrode acting as cathode is less than its reversible value due to concentration polarization.

Type D: Fill in the Blanks

15.61 In an electrochemical cell, oxidation occurs at ———— while reduction occurs at ————.

15.62 For a cell reaction to occur spontaneously in a given direction, the e.m.f. of the cell should be ————.

15.63 The equilibrium constant (K) for a cell reaction is related to the e.m.f. as $\log K =$ ————.

15.64 Over voltage is observed in case of cells working under ———— conditions.

15.65 The concentration dependence of the e.m.f. of a cell is given by ———— equation.

ANSWERS

Numerical Problems

15.2 $Zn(s) + Hg_2Cl_2(s) = 2Hg(l) + Zn^{2+} + 2Cl^-$; 0.763 V *15.3* (a) 1.0225 (b) 0.260 (c) 0.904 *15.4* $E°$ is negative (− 0.824) and the reaction is nonspontaneous *15.5* (a) spontaneous (b) spontaneous (c) nonspontaneous *15.6* Both (a) and (b) *15.7* (a) 0.327 V (b) 0.971 *15.8* (a) decreases by 0.0295 V (b) increases by 0.0295 V *15.9* 0.294, −28.4 kJ. *15.10* (a) −189.5 kJ (b) −131.2 kJ *15.11* 0.2814 *15.12* −103.45 kJ, 27.985 J, 111.79 kJ *15.13* −159.0 kJ, 7.4×10^{27} *15.14* −0.816 V, 78.718 kJ mol^{-1} *15.15* 1.345 *15.16* 2.43×10^{-6} *15.17* −0.475 *15.18* 0.335 *15.19* 1.175 V *15.20* 0.1832 V

Quiz Questions

15.21 (d) *15.22* (b) *15.23* (b) *15.24* (c) *15.25* (b) *15.26* (a) *15.27* (b) *15.28* (d) *15.29* (c) *15.30* (a) *15.31* (a) *15.32* (c) *15.33* (c) *15.34* (b) *15.35* (b) *15.36* (a) *15.37* (d) *15.38* (a) *15.39* (d) *15.40* (c) *15.41* (a) *15.42* (a) *15.43* (c) *15.44* (b) *15.45* (b) *15.46* (a) *15.47* (a) *15.48* (a) *15.49* (d) *15.50* (c) *15.51* True *15.52* False *15.53* False *15.54* True *15.55* False *15.56* False *15.57* False *15.58* False *15.59* True *15.60* False *15.61* Anode, cathode *15.62* +ve *15.63* $nFE/2.303\,RT$ *15.64* irreversible *15.65* Nernst

16

Atomic Structure

Dalton (1808) regarded the atom as an individual particle of an element, but it was found that even the atom is made up of subatomic particles. Many experimental observations and theoretical developments have led to the unfolding of atomic structure.

16.1 FUNDAMENTAL PARTICLES CONSTITUTING ATOMS

The three fundamental particles* of matter constituting all atoms are electrons, protons and neutrons. The mass and charge of these particles have been determined experimentally and are given below:

Particle	*Mass*	*Charge*
Electron	9.109×10^{-31} kg (1/1837th of a H atom)	-1.602×10^{-19}C (one unit negative charge, $-e$)
Proton	1.673×10^{-27} kg (same as H atom)	(one unit positive charge, $+e$)
Neutron	1.673×10^{-27} kg (same as H atom)	no charge

16.2 RUTHERFORD'S NUCLEAR MODEL OF THE ATOM

Rutherford and his co-workers studied the scattering of α-particles (He^{2+} ions) by thin metallic foils. The results of the scattering experiments led Rutherford to propose the nuclear model of the atom. According to this model:

1. An atom consists of an extremely small, dense positively charged part called the *nucleus*, which is present at the centre of the atom (size $\approx 10^{-15}$ m, density $\approx 4 \times 10^{11}$ kg m^{-3} or 10^8 times that of water).

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*These days, quarks are considered to be the ultimate particles. But, for the extra-nuclear structure, it is sufficient to consider the atom as constituted of electrons and a positively charged nucleus consisting of protons and neutrons.

2. The nucleus is surrounded by negatively charged electrons which revolve around the nucleus.
3. Most of the space in the atom (between the nucleus and electrons) is empty.

16.3 ATOMIC NUMBER AND MASS NUMBER

The number of unit positive charges carried by the nucleus of an atom is called its *atomic number* (Z). The atomic number of an element is equal to the number of protons in the nucleus or the number of electrons in the extranuclear part in an atom.

The sum of the neutrons and protons in an atom is known as the *mass number* (A).

16.4 NATURE AND CHARACTERISTICS OF RADIATION

Visible light, ultraviolet light, infrared radiation, X-rays, etc. are different forms of radiation. Maxwell proposed that all forms of radiation propagate through space in the form of waves which have electric and magnetic fields associated with them. Hence, these are called *electromagnetic radiations*.

Wave motion is characterised by the following quantities:

Wavelength (λ)

The distance between two corresponding points (crests or troughs) on adjacent waves. It is expressed in m or A° ($1A° = 10^{-10}$ m = 0.1 nm).

Frequency (v)

The number of waves which pass through a given point in one second (expressed in s^{-1} or Hertz, Hz).

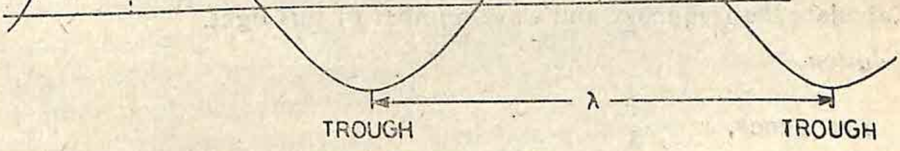


FIG. 16.1 *Wave motion*

Velocity (c)

The distance travelled by a wave in one second (expressed in m s^{-1}).

Amplitude (a)

The height of a crest or depth of a trough.

Wave number $(\bar{\nu})$

The number of wavelengths per centimetre, equal to the reciprocal of wavelength. Thus,

$$\bar{\nu} = \frac{1}{\lambda} \text{ cm}^{-1} \text{ or } kaysers$$

The relationship between wavelength (λ) and frequency (ν) is

$$\lambda \times \nu = c \tag{16.1}$$

where c is the velocity of light $(3 \times 10^8 \text{ m s}^{-1})$

A characteristic feature of electromagnetic radiation is that all types of radiations travel in vacuum with the same speed as that of light.

16.5 ELECTROMAGNETIC SPECTRA

The arrangement of different types of electromagnetic radiations in the order of increasing wavelengths (or decreasing frequencies) is called an *electromagnetic spectra*.

This is shown in Fig. 16.2 (visible region shown separately).

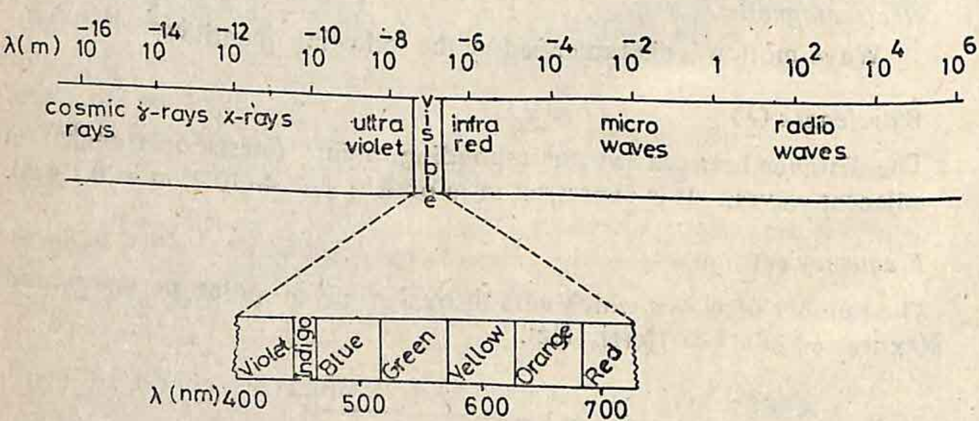


FIG. 16.2 *Electromagnetic spectrum*

EXAMPLE 16.1 (SI Units) The wavelength of blue light is 480 nm. Calculate the frequency and wave number of this light.

Solution

$$\text{Frequency, } \nu = \frac{c}{\lambda}$$

$$c = 3 \times 10^8 \text{ m s}^{-1}, \quad \lambda = 480 \text{ nm} = 480 \times 10^{-9} \text{ m}$$

$$\therefore \quad \nu = \frac{3 \times 10^8 \text{ m s}^{-1}}{480 \times 10^{-9} \text{ m}}$$

$$= 6.25 \times 10^{14}\ \mathrm{s^{-1}}\ \text{or}\ 6.25 \times 10^{14}\ \mathrm{Hz}$$

$$\text{Wave number, } \bar{\nu} = \frac{1}{\lambda} = \frac{1}{480 \times 10^{-7}\ \mathrm{cm}}$$

$$= 2.08 \times 10^{4}\ \mathrm{cm^{-1}} = 2.08 \times 10^{4}\ \text{kayser}$$

EXAMPLE 16.2 (SI Units) The frequency of a wave of light is $5 \times 10^{14}\ \mathrm{s^{-1}}$. Calculate the wavelength and wave number associated with the light.

Solution

$$\text{Wavelength, } \lambda = \frac{C}{\nu}$$

$$c = 3 \times 10^{8}\ \mathrm{m\ s^{-1}}, \quad \nu = 5 \times 10^{14}\ \mathrm{s^{-1}}$$

$$\therefore \quad \lambda = \frac{3 \times 10^{8}\ \mathrm{m\ s^{-1}}}{5 \times 10^{14}\ \mathrm{s^{-1}}}$$

$$= 6 \times 10^{-7}\ \mathrm{m} = 600\ \mathrm{nm}$$

$$\text{Wave number, } \bar{\nu} = \frac{1}{\lambda}$$

$$= \frac{1}{6.0 \times 10^{-5}\ \mathrm{cm}} = 1.67 \times 10^{4}\ \mathrm{cm^{-1}}$$

16.6 ATOMIC SPECTRA

When white light is allowed to pass through a prism, it spreads into a series of colour bands called a *spectrum*. This is a continuous spectrum. However, the spectra of atoms are not continuous. When the gases or vapours of chemical substances are heated by an electric spark or on a bunsen flame, these decompose into atoms in excited states. When the light emitted from them is analysed with the help of a spectroscope, an emission spectra is obtained, which consists of a series of sharp well-defined lines, each corresponding to a definite wavelength. A spectrum of this type is referred to as *line spectrum*. The wavelengths of the various lines in a line spectrum are unique to each atom or ion and are different from those of others.

On the other hand, when a continuous electromagnetic radiation is allowed to pass through an atomic system and the transmitted light is analysed, a spectrum is obtained in which dark lines are observed in an otherwise continuous spectrum. These dark lines indicate that radiations of corresponding wavelengths have been absorbed, by the substance, from white light. The spectrum obtained is called an *absorption spectrum*. It may be noted that, for an element in the atomic form, the dark lines appear at exactly the same places as the lines in the emission spectrum.

16.7 OLD QUANTUM THEORY

The wave concept of light was found inadequate while trying to explain phenomena like the distribution of energy in black bodies and the photoelectric effect.

Black Body Radiation

An ideal black body is defined as a perfect absorber and emitter. When such a body is heated, it emits light, the colour of which changes from red to yellow and finally white at very high temperatures. It has a characteristic distribution. At each temperature there is a wavelength at which the intensity of radiation is maximum (λ_{max}). This maximum shifts to a lower wavelength as the temperature is increased.

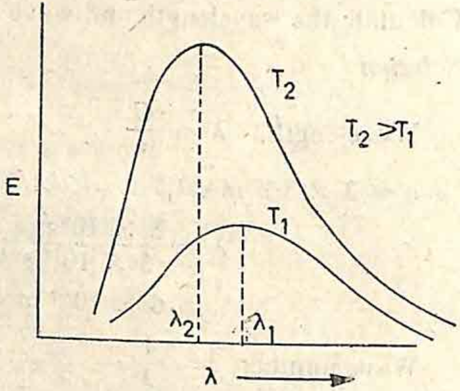


FIG. 16.3 *Intensity of black body as a function of* λ

Photoelectric Effect

The phenomenon of ejection of electrons from metal surfaces when light of suitable frequency strikes it is called the photoelectric effect. The ejected electrons are called photo electrons.

Experimental studies under different conditions lead to the following observations:

1. For each metal, there is a characteristic *threshold frequency* (ν_0) at which incident light can eject electrons. Light of frequency less than ν_0 cannot eject electrons, no matter how long it falls on the surface or how high its intensity is.

2. The kinetic energy of emitted electrons depends upon the frequency ($\nu > \nu_0$) of the incident radiation, and is independent of its intensity.

3. The number of electrons ejected from the metal surface depends upon the intensity of incident radiation ($\nu > \nu_0$).

The failure of the classical electromagnetic theory of radiation to explain the above phenomenaled to the postulation of the quantum theory of radiation.

16.8 PLANCK'S QUANTUM THEORY OF RADIATION

The main postulates of Planck's Quantum theory (1901) are:

1. Radiant energy is not emitted or absorbed continuously, but *discontinuously* in the form of small packets of energy called *quanta.* The quantum of light energy is called *photon.*

2. The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation, i.e.

$$\varepsilon \propto \nu \quad \text{or} \quad \varepsilon = h\nu \tag{16.2}$$

where h is called *Planck's constant* ($h = 6.625 \times 10^{-27}$ erg s or 6.625×10^{-34} J s).

3. A body can emit or absorb energy in terms of integral multiples of quantum, i.e. $E = nh\nu$ where $n = 1, 2, 3, \ldots$.

Planck solved the problem of black body radiation and Einstein (1905) sucessfully used this concept to explain the photoelectric effect and the specific heats of solids.

According to Einstein, when a photon of energy $h\nu$ strikes a metal surface, some of its energy (W, called work function) is used up to remove an electron from the metal and the remaining energy is imparted to the ejected electron as kinetic energy ($\frac{1}{2}mv^2$). This gives

$$h\nu = W + \tfrac{1}{2}mv^2 = h\nu_0 + \tfrac{1}{2}mv^2 \tag{16.3}$$

A certain minimum frequency (corresponding to the work function, $W = h\nu_o$) known as the threshold frequency is necessary to knock out the electron from the metal. Further, the kinetic energy will increase with increase in the frequency of radiation.

EXAMPLE 16.3 Calculate the energy of a photon of wave length 4500 Å.

Solution

$$\varepsilon = h\nu$$

$$= \frac{hc}{\lambda} \qquad \left(\nu = \frac{c}{\lambda}\right)$$

$$\lambda = 4500\text{Å} = 4500 \times 10^{-10}\ \text{m},\ c = 3 \times 10^8\ \text{m s}^{-1},$$

$$h = 6.625 \times 10^{-34}\ \text{J s}$$

$$= \frac{(6.625 \times 10^{-34}\ \text{J s}) \times (3 \times 10^8\ \text{m s}^{-1})}{(4500 \times 10^{-10}\ \text{m})}$$

$$= 4.42 \times 10^{-19}\ \text{J}$$

EXAMPLE 16.4 The threshold frequency for photoelectric emission of electrons from platinum is $1.3 \times 10^{15}\ \text{s}^{-1}$.

(a) What is the minimum energy that photons of a particular radiation must possess in order to produce the photoelectric effect with platinum metal ?

(b) Will a light of 400 nm eject electrons from platinum ?

Solution (a) The minimum energy of photon required to eject electrons

$$\varepsilon = h\nu_0$$

$$h = 6.625 \times 10^{-34}\ \text{J s} \quad , \quad \nu_0 = 1.3 \times 10^{15}\ \text{s}^{-1}$$

$$\begin{aligned}\varepsilon &= (6.625 \times 10^{-34}\ \text{J s}) \times (1.3 \times 10^{15}\ \text{s}^{-1})\\ &= 8.61 \times 10^{-19}\ \text{J}\end{aligned}$$

(b) To eject electrons from platinum, the energy of the incident light must be equal to or greater than 8.61×10^{-19} J.

The energy of photon of light of wavelength 400 nm

$$\begin{aligned}\varepsilon &= \frac{hc}{\lambda}\\ &= \frac{(6.625 \times 10^{-34}\ \text{J s}) \times (3 \times 10^{8}\ \text{m s}^{-1})}{400 \times 10^{-9}\ \text{m}}\\ &= 4.97 \times 10^{-19}\text{J}\end{aligned}$$

Since the energy of photon of light of wavelength 400 nm (4.97×10^{-19} J) is less than 8.61×10^{-19} J, ejection of electrons will not occur.

EXAMPLE 16.5 Calculate the velocity of electrons ejected from sodium metal surface when radiation of 300 nm falls on it. The threshold wavelength of sodium metal is 650 nm (mass of electron = 9.11×10^{-31} kg).

Solutions

$$h\nu = h\nu_0 + \tfrac{1}{2}mv^2$$

$$\text{or}\quad \tfrac{1}{2}mv^2 = h\nu - h\nu_0$$

$$\text{or}\quad \nu^2 = \frac{2h\,(\nu - \nu_0)}{m}$$

$$\nu = \frac{c}{\lambda} = \frac{3 \times 10^{8}\ \text{m s}^{-1}}{300 \times 10^{-9}\ \text{m}} = 1.0 \times 10^{15}\ \text{s}^{-1}$$

$$\nu_0 = \frac{c}{\lambda_0} = \frac{3 \times 10^{8}\ \text{m s}^{-1}}{650 \times 10^{-9}\ \text{m}} = 0.46 \times 10^{15}\ \text{s}^{-1}$$

$$m = 9.11 \times 10^{-31}\ \text{kg}, \qquad h = 6.625 \times 10^{-34}\ \text{J s}$$

$$\therefore\ v^2 = \frac{2 \times (6.625 \times 10^{-34}\ \text{J s}) \times (1.0 - 0.46) \times 10^{15}\ \text{s}^{-1}}{9.11 \times 10^{-31}\ \text{kg}}$$

$$= 7.854 \times 10^{11}$$

$$\text{or } v = 8.86 \times 10^{5}\ \text{m s}^{-1}$$

EXAMPLE 16.6 When radiation of 375 nm was allowed to strike a metallic surface, a voltage of 0.76V was required to stop the ejection of electrons. Calculate

(a) work function
(b) threshold frequency
(c) velocity of photoelectrons

Solution When the photoelectric emission stops, the kinetic energy of the ejected electrons becomes equal to the electrical work done Ve (where V is the external voltage and e is the electronic charge), i.e.

$$\text{K.E.} = \tfrac{1}{2}mv^2 = Ve$$

$$e = 1.6 \times 10^{-19}\ \text{C},\ V = 0.76\ \text{V}$$

$$\text{K.E.} = (0.76\ \text{V}) \times (1.6 \times 10^{-19}\ \text{C})$$

$$= 1.216 \times 10^{-19}\ \text{V C} = 1.216 \times 10^{-19}\ \text{J} \qquad \text{(i)}$$

The energy of the photon striking the metallic surface

$$\varepsilon = h\nu = \frac{hc}{\lambda} = \frac{(6.625 \times 10^{-34}\ \text{J s}) \times (3.0 \times 10^{8}\ \text{m s}^{-1})}{(375 \times 10^{-9}\ \text{m})}$$

$$= 5.3 \times 10^{-19}\ \text{J}$$

According to Einstein's relation,

$$E = E_0 + \tfrac{1}{2} mv^2 \qquad \text{(ii)}$$

(a) Work function, $E_0 = E - \tfrac{1}{2} mv^2$

$$= 5.3 \times 10^{-19} - 1.216 \times 10^{-19}$$

$$= 4.084 \times 10^{-19}\ \text{J}$$

or $E_0 = (4.084 \times 10^{-19}\ \text{J}) \times (6.25 \times 10^{18}\ \text{eV J}^{-1})$

$$= 2.55\ \text{eV} \qquad [1\ \text{J} = 6.25 \times 10^{18}\ \text{eV}]$$

(b) Threshold frequency $\nu_0 = \dfrac{E_0}{h}$

$$= \frac{4.084 \times 10^{-19}\ \text{J}}{6.625 \times 10^{-34}\ \text{J s}} = 6.16 \times 10^{14}\ \text{s}^{-1}$$

(c) From (i) $\quad \tfrac{1}{2} mv^2 = 1.216 \times 10^{-19}\ \text{J}$

or $\quad v^2 = \dfrac{2 \times 1.216 \times 10^{-19}\ \text{J}}{9.11 \times 10^{-31}\ \text{kg}}$

$$= 2.67 \times 10^{11}$$

$\therefore \quad v = 5.17 \times 10^{5}\ \text{m s}^{-1}$

16.9 THE BOHR THEORY OF THE HYDROGEN ATOM

The basic postulates of Bohr's theory (1913) are:

1. An electron in an atom revolves around the nucleus only in certain allowable circular orbits having definite energies. These are numbered 1, 2, 3, 4, . . . or, alternatively, K, L, M, N, . . ., etc.

2. As long as the electron remains in a particular orbit, it does not lose or gain energy (stationary orbit).

3. Energy is emitted or absorbed in discrete amounts by an atom only when the electron jumps from one orbit to another.

4. The angular momentum of an electron revolving around the nucleus in an orbit is quantized, i.e. must be an integral multiple of $h/2\pi$

$$mvr = n\,\frac{h}{2\pi} \qquad (16.4)$$

On the basis of his postulates, Bohr derived a mathematical expression for the energy of an electron moving in a particular orbit of a hydrogen atom. He imagined the hydrogen atom as a system consisting of a single electron of mass m and negative charge, $-e$ revolving in a circular orbit. The energy of the electron in the nth orbit has been found to be

$$E_n = \frac{-2\pi^2 \mu e^4}{n^2h^2} \tag{16.5}$$

where μ is the reduced mass of the system

$$\mu = \frac{mM}{m+M} \approx m$$

Hence, using m,

$$E_n = \frac{-2\pi^2 me^4}{n^2h^2} \tag{16.6}$$

Now, in case of hydrogen-like atoms (He^+, Li^{2+}, . . .) where Z is the nuclear charge, relation (16.6) becomes

$$E_n = \frac{-2\pi^2 Z^2 me^4}{n^2h^2} \tag{16.7}$$

Similarly, Bohr derived the radius of orbit and the velocity of an electron in any orbit,

$$r_n = \frac{n^2h^2}{4\pi^2 me^2 Z} \tag{16.8}$$

and

$$v_n = \frac{2\pi Z e^2}{nh} \tag{16.9}$$

In esu units, the electrostatic force of attraction between the electron and nucleus is equal to e^2/r^2, but in SI units this force is given by $(1/4\pi\varepsilon_0)$ e^2/r^2 where ϵ_0 is a constant called the *permitivity* of the medium. Its numerical value is 8.8542×10^{-12} $C^2N^{-1}m^{-2}$. Therefore, the relations for the energy, radius and velocity of electron in SI units becomes

$$E_n = -\frac{2\pi^2 m Z^2e^4}{n^2h^2}\left(\frac{1}{4\pi\varepsilon_0}\right)^2 \tag{16.10}$$

$$r_n = \frac{(4\pi^2\varepsilon_0)\, n^2h^2}{4\pi^2 m e^2Z} \tag{16.11}$$

$$v_n = \frac{2\pi Z e^2}{(4\pi\varepsilon_0)nh} \tag{16.12}$$

Substituting the known values for various constants, we get

$$E_n = \frac{-2.18 \times 10^{11}}{n^2} \text{ erg per atom}$$

or

$$-\frac{2.18 \times 10^{-18}}{n^2} \text{ J per atom}$$

or

$$E_n = -\frac{13.63}{n^2} \text{ eV per atom}$$

or

$$E_n = -\frac{313.6}{n^2} \text{ kcal mol}^{-1} = \frac{-1312}{n^2} \text{ kJ mol}^{-1}$$

According to Bohr's model, an electron in a hydrogen atom can go from one energy level to another only in jumps. As a result, an atom can absorb or emit energy equal to the difference in energies between the two energy levels. For example, if an electron comes back from an energy level of energy E_2 to an energy level of energy E_1,

$$E_2 - E_1 = h\nu$$

or
$$\nu = \frac{E_2 - E_1}{h} \tag{16.13}$$

or
$$\frac{c}{\lambda} = \frac{E_2 - E_1}{h}$$

or
$$\lambda = \frac{hc}{E_2 - E_1} \tag{16.14}$$

Thus, each transition will produce a light of definite wavelength. For example, in the hydrogen atom, when the electron jumps from energy levels higher than $n = 1$, i.e. $n = 2, 3, 4, 5, \ldots$, to the $n = 1$ energy level, the emitted light falls in the ultraviolet region. The lines obtained are called the *Lyman series*. Some prominent series observed for hydrogen atoms are described below:

Series	*Region*	*Transition*
Lyman	ultraviolet	From $n = 2, 3, 4, 5, \ldots$ to $n = 1$
Balmer	visible	From $n = 3, 4, 5, 6, \ldots$ to $n = 2$
Paschen	infrared	From $n = 4, 5, 6, 7, \ldots$ to $n = 3$
Brackett	infrared	From $n = 5, 6, 7, 8, \ldots$ to $n = 4$
Pfund	infrared	From $n = 6, 7, 8, \ldots$ to $n = 5$

16.10 FREQUENCY AND WAVE NUMBER OF EMITTED RADIATIONS

The frequency (ν) and wave number ($\bar{\nu}$) of the spectral line, when an electron jumps down from energy level n_2 to n_1, are obtained as

$$\nu = 3.289 \times 10^{15} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{s}^{-1} \tag{16.15}$$

and
$$\bar{\nu} = \frac{1}{\lambda} = 109678.3 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{cm}^{-1} \tag{16.16}$$

The above relations obtained from Bohr's model were similar to one proposed by Ritz as

$$\bar{\nu} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{16.17}$$

where R is Rydberg's constant and is equal to 109714 cm^{-1}.

EXAMPLE 16.7 Calculate,

(a) the radii of the first and second Bohr orbits of hydrogen

(b) the velocity of the electron in these two orbits

Solution (a) Bohr's radius is given by the relation

$$r_n = \frac{n^2h^2}{4\pi^2me^2}$$

$$m = 9.11 \times 10^{-28}\ \text{g},\ h = 6.625 \times 10^{-27}\ \text{erg s}$$
$$e = 4.8 \times 10^{-10}\ \text{e.s.u.}$$

$$\therefore \quad r_n = \frac{n^2 \times (6.625 \times 10^{-27})^2}{4 \times (3.14)^2 \times (9.11 \times 10^{-28}) \times (4.8 \times 10^{-10})^2}$$
$$= 0.53 \times 10^{-8}\, n^2\ \text{cm} = 0.53\ \text{n}^2\ \text{Å}$$

For the first orbit, $n = 1$

$$r_1 = 0.53 \times 1^2 = 0.53\ \text{Å}$$

For the second orbit, $n = 2$

$$r_2 = 0.53 \times 2^2 = 2.12\ \text{Å}$$

(b) Velocity of the electron in an orbit is given by

$$v_n = \frac{2\pi e^2}{nh}$$

Substituting values, we get

$$v_n = \frac{2 \times 3.14 \times (4.8 \times 10^{-10})^2}{n \times (6.625 \times 10^{-27})}$$
$$= \frac{2.18 \times 10^8}{n}\ \text{cm s}^{-1}$$

Now, for the first orbit, $n = 1$

$$v_1 = 2.18 \times 10^8\ \text{cm s}^{-1}$$

For second orbit, $n = 2$

$$v_2 = \frac{2.18 \times 10^8}{2} = 1.09 \times 10^8\ \text{cm s}^{-1}$$

EXAMPLE 16.8 (SI Units) Calculate the energies of the first four Bohr orbits of the hydrogen atom. Calculate the frequencies of the light emitted when the electron jumps from the fourth orbit to the third, second and first respectively.

(Permitivity $= 8.85 \times 10^{-12}\ \text{C}^2\text{N}^{-1}\text{m}^{-2}$)

Solution Energy of an electron in the nth orbit of Bohr is given by

$$E_n = -\frac{2\pi^2 m Z^2 e^4}{n^2h^2}\left(\frac{1}{4\pi\varepsilon_0}\right)^2$$

$$m = 9.11 \times 10^{-31}\ \text{kg},\ Z = 1,\ e = 1.602 \times 10^{-19}\text{C},$$
$$h = 6.625 \times 10^{-34}\ \text{J s}$$
$$\varepsilon_0 = 8.85 \times 10^{-12}\text{C}^2\text{N}^{-1}\ \text{m}^{-2},\ Z = 1$$

$$\therefore \quad E_n = \frac{-2 \times (3.14)^2 \times (9.11 \times 10^{-31}\ \text{kg}) \times (1^2 \times 1.602 \times 10^{-19}\text{C})^4}{n^2(6.625 \times 10^{-34}\ \text{J s})^2 \times (4 \times 3.14 \times 8.85 \times 10^{-12}\text{C}^2\text{N}^{-1}\text{m}^{-2})^2}$$
$$= \frac{-2.18 \times 10^{-18}\ \text{J}}{n^2}$$
$$= \frac{-2.10 \times 10^{-8}\ \text{J} \times 6.022 \times 10^{23}\ \text{mol}^{-1}}{n^2}$$

$$= \frac{-13.12 \times 10^2}{n^2} \text{ kJ mol}^{-1}$$

For the first orbit, $E_1 = -1312 \text{ kJ mol}^{-1}$

For the second orbit, $E_2 = \frac{-1312}{2^2} = -328 \text{ kJ mol}^{-1}$

For the third orbit, $E_3 = \frac{-1312}{3^2} = -145.8 \text{ kJ mol}^{-1}$

For the fourth orbit, $E_4 = \frac{-1312}{4^2} = -82 \text{ kJ mol}^{-1}$

When the electron jumps from a higher to a lower orbit, the energy given out

$$\Delta E = E_h - E_l = h\nu$$

or, frequency of light emitted

$$\nu = \frac{E_h - E_l}{h}$$

(i) When the electron jumps from the fourth orbit to the third

$$\nu = \frac{E_4 - E_3}{h}$$

$$= \frac{[-82.0-(-145.8)] \text{ k J mol}^{-1}}{3.98 \times 10^{-13} \text{ kJ mol}^{-1} \text{ s}}$$

$$[h = 6.625 \times 10^{-34} \text{ J s} = 3.98 \times 10^{-13} \text{ kJ mol}^{-1} \text{ s}]$$

$$= 1.603 \times 10^{14} \text{ s}^{-1}$$

(ii) When the electron jumps from the fourth orbit to the second,

$$= \frac{[-145.8 - (-328.0)] \text{ kJ mol}^{-1}}{3.98 \times 10^{-13} \text{ kJ mol}^{-1} \text{ s}}$$

$$= 4.58 \times 10^{14} \text{ s}^{-1}$$

(iii) When the electron jumps from the fourth orbit to the first,

$$= \frac{[-328 - (-1312)] \text{ kJ mol}^{-1}}{3.98 \times 10^{-13} \text{ kJ mol}^{-1} \text{ s}}$$

$$= 2.47 \times 10^{15} \text{ s}^{-1}$$

16.11 FAILURES OF OLD QUANTUM THEORY

Bohr's theory of atomic structure based upon the old quantum theory was quite successful in explaining the spectra of hydrogen and hydrogen-like atoms (He^+, Li^{2+}). However, it could not explain, the spectra of other multi-electron atoms and the intensity of the spectral lines. Although the theory was extended to include elliptical orbits, it could not go very far. Ultimately, it had to be abandoned as certain irrational assumptions had to be made to explain experimental observations.

16.12 DUAL NATURE OF MATTER AND LIGHT

Louis de Broglie (1924) suggested that material particles (such as electrons, protons, atoms and molecules) like light, exhibit a dual character (wave as well as particle). He showed that the wavelength associated with a particle is related to its momentum p by the relation

$$\lambda = \frac{h}{p} \tag{16.18}$$

For particles of mass m and velocity v ($v < c$), $p = mv$. Hence,

$$\lambda = \frac{h}{mv} \tag{16.19}$$

It may be noted that the dual nature of matter has significance for microscopic bodies only. For heavy bodies, the wavelengths of associated waves are very small compared to their sizes. Therefore, the motion of macroscopic bodies is described by laws of classical mechanics. The wave nature of matter was experimentally verified by C.J. Davisson and L.H. Germer (1927), and G.P. Thompson (1928).

EXAMPLE 16.9 Calculate the de Broglie wavelength associated with a ball weighing 150 g thrown with a velocity of 3×10^3 cm s^{-1}.

Solution

$$\lambda = \frac{h}{mv}$$

$$h = 6.625 \times 10^{-27}\ \text{erg s},\ m = 150\ \text{g},\ v = 3 \times 10^3\ \text{cm s}^{-1}$$

$$\therefore \quad \lambda = \frac{(6.625 \times 10^{-27}\ \text{erg s})}{(150\ \text{g}) \times (3 \times 10^3\ \text{cm s}^{-1})}$$

$$= 1.47 \times 10^{-32}\ \text{cm} = 1.47 \times 10^{-24}\ \text{Å}$$

EXAMPLE 16.10 (SI Units) Calculate the de Broglie wavelength of an electron accelerated through a potential difference of 1×10^4 V.

Solution

Kinetic energy of electrons = Potential energy gained by each electron

i.e. $\frac{1}{2} mv^2 = eV$

or

$$v = \sqrt{\frac{2\,eV}{m}}$$

$$V = 1\times10^4\text{V}, \quad e = 1.602\times10^{-19}\text{C}, \quad m = 9.11\times10^{-31}\ \text{kg}$$

$$\therefore \quad v = \left(\frac{2 \times (1.602 \times 10^{-19}\text{C}) \times (1 \times 10^4\text{V})}{9.11 \times 10^{-31}\ \text{kg}}\right)^{\frac{1}{2}}$$

$$= 5.93 \times 10^7\ \text{m s}^{-1} \qquad [\text{CV} = \text{J} = \text{kg m}^2\ \text{s}^{-2}]$$

Now, $$\lambda = \frac{h}{mv}$$

$$h = 6.625 \times 10^{-34}\text{J s},\ m = 9.11 \times 10^{-31}\ \text{kg},$$

$$v = 5.93 \times 10^7 \text{ m s}^{-1}$$

$$\therefore \quad \lambda = \frac{6.625 \times 10^{-34} \text{ J s}}{9.11 \times 10^{-31}\text{kg} \times 5.93 \times 10^7 \text{ m s}^{-1}}$$

$$= 1.226 \times 10^{-11} \text{ m} = 0.0123 \text{ nm}$$

16.13 HEISENBERG'S UNCERTAINTY PRINCIPLE

Heisenberg (1927) pointed out that it is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty. He showed that the product of uncertainties in the measurement of position (Δx) and momentum (Δp) is expressed mathematically by the relation:

$$\Delta x \times \Delta p \approx \frac{h}{2\pi} \tag{16.20}$$

This means that if we wish to determine the position of an electron with great accuracy (decrease the magnitude of Δx), the corresponding uncertainty in momentum will be large, and vice versa.

The value of h is so small that the Heisenberg principle seems to be of little consequence for large bodies.

Example 16.11 The uncertainty in the momentum of a particle is found to be 2.5×10^{-16} g cm s^{-1}. With what accuracy can its position be determined?

Solution According to Heisenberg's uncertainty principle

$$\Delta x \times \Delta p \approx \frac{h}{2\pi}$$

$$\Delta p = 2.5 \times 10^{-16} \text{ g cm s}^{-1}, \; h = 6.625 \times 10^{-27} \text{ erg s}$$

$$\therefore \quad \Delta x \approx \frac{h}{2\pi \times \Delta p}$$

$$\approx \frac{6.625 \times 10^{-27} \text{ erg s}}{2 \times 3.14 \times 2.5 \times 10^{-16} \text{ g cm s}^{-1}}$$

$$\approx 4.22 \times 10^{-12} \text{ cm} \qquad [\text{erg} = \text{g cm}^2 \text{ s}^{-2}]$$

Thus, uncertainty in position = 4.22×10^{-12} cm

Example 16.12 (SI Units) Calculate the uncertainty in velocity of an electron when the uncertainty in position is 0.1 nm.

Solution

$$\Delta x \times \Delta p \approx \frac{h}{2\pi}$$

$$\Delta x = 0.1 \text{ nm} = 0.1 \times 10^{-9} \text{ m} = 1 \times 10^{-10} \text{ m}$$

$$\therefore \quad \Delta p = \frac{6.625 \times 10^{-34} \text{ J s}}{2 \times 3.14 \times (1 \times 10^{-10} \text{ m})} \qquad [\text{J} = \text{kg m}^2 \text{ s}^{-2}]$$

$$= 1.055 \times 10^{-24}\ \text{kg m s}^{-1}$$

Now $\Delta p = m\Delta v$

or $$\Delta v = \frac{\Delta p}{m}$$

$$= \frac{1.055 \times 10^{-24}\ \text{kg m s}^{-1}}{9.11 \times 10^{-31}\ \text{kg}}$$

$$= 1.16 \times 10^{6}\ \text{m s}^{-1}$$

Uncertainty in velocity $= 1.16 \times 10^{6}\ \text{m s}^{-1}$

16.14 THE SCHRÖDINGER WAVE EQUATION

In the light of the uncertainty principle and the dual nature of light, E. Schrödinger proposed an equation (called the Schrödinger equation) for getting information on the structure of atoms and molecules. For a single electron moving in three dimensions in a potential field V, the Schrödinger wave equation reduces to

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

or $$\nabla^2\psi + \frac{8\pi^2\mu}{h^2}(E - V)\psi = 0$$

where $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ is called the Laplacian operator.

E is the total energy, V is the potential energy ($V = -e^2/r$ or $-e^2/4\pi\varepsilon_0 r$ for hydrogen atom), ψ (Greek letter psi) is called the wave function, $\frac{\partial^2\psi}{\partial x^2}$ refers to the partical second derivative of ψ wrt x and μ is the reduced mass $\left(\mu = \frac{mM}{m + M} \approx m\right)$ for the system.

The Schrödinger wave equation has physically valid solutions only for certain values of E's (allowed energies). These are called *eigen values* and the corresponding wave functions ψ's are called *eign functions*. ψ must be a well-behaved function and fulfil the following conditions:

1. ψ must have a finite value.
2. ψ must be single valued.
3. ψ must be continuous.

The importance of the Schrödinger wave equation lies in its validity and the agreement of calculated values with experimental facts for atomic and molecular systems. The Schrödinger wave equation, in fact, marked the beginning of a new era in the history of science.

16.15 PHYSICAL SIGNIFICANCE OF ψ AND ψ^2

ψ is a mathematical function and has no physical meaning by itself. But the square of the wave function, ψ^2, corresponds to the probability density at that point. Now, if dV is a finite volume ($dx\ dy\ dz$) then $\psi^2 dV$ gives the probability of finding the system (in this case electron) in the volume dV between the coordinates x and $x + dx$, y and $y + dy$ and z and $z + dz$.

16.16 WAVE FUNCTIONS FOR HYDROGEN ATOM

For the solution of the Schrödinger wave equation for the hydrogen atom, it is more convenient to transform the equation to polar coordinates, r, θ and ϕ (which are related to the Cartesian coordinates x, y and z, as shown in Fig. 16.4) as

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2} + \frac{8\pi^2\mu}{h^2}\left(E + \frac{e^2}{r}\right)\psi = 0 \qquad (16.21)$$

The wave function can be resolved into two factors and leads to the introduction of three quantum numbers (n, l and m) which are discussed later (Section 16.17).

Radial Wave Function $R(r)$

This gives the distribution of electrons, as a function of distance (r) from the nucleus and depends upon two quantum numbers n and l.

Angular Wave Function [$Y(\theta, \phi)$]

It depends upon the angles θ and ϕ and is a function of quantum numbers l and m.

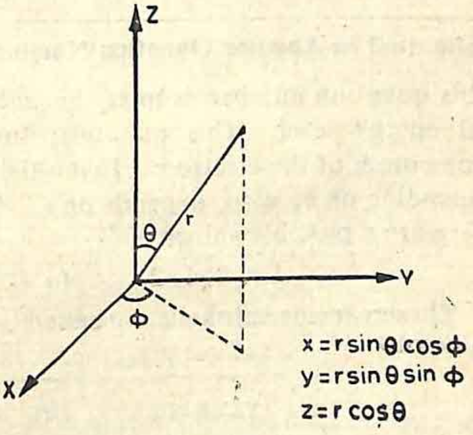


FIG. 16.4

The complete wave function is expressed as the product of radial and angular parts as

$$\psi(r, \theta, \phi) = R(r)\ Y(\theta, \phi) \qquad (16.22)$$

This wave function represents an orbital.

Orbital Approximation

For a multielectron atom it may be considered as the electrons moving in their individual orbitals in the field of other electrons. This model is called an orbital approximation. Here, the total wave function can be represented by the product of orbitals ψ_i's. Each orbital depends on the quantum numbers n, l, m and s. More accurately the wave function is represented by a Slater determinant whose elements are ψ_i's occupied by different electrons.

16.17 QUANTUM NUMBERS

The solution of the Schrödinger wave equation gives rise to three quantum numbers, n, l and m. Each electron in an atom is characterized by a set of definite values of these numbers. In addition to these, another quantum number s is also needed, which specifies the spin of the electron. The implications of the four quantum numbers are discussed below.

Principal Quantum Number (n)

This quantum number determines the *main energy level* or *shell* in which the electron is present. The average distance of the electron from the nucleus, and the energy associated, depend on n. It can have whole-number values as

$$n = 1, 2, 3, 4, \ldots$$

Azimuthal or Angular Quantum Number (l)

This quantum number denotes the *sublevel* or *subshell* in a given principal energy level. This quantum number is related to the angular momentum of the electron. In multielectron atoms, the energy, besides depending on n, also depends on l. Corresponding to each value of n there are n possible values of l

$$l = 0, 1, 2, \ldots, (n - 1)$$

These various subshells are called s, p, d, f, . . . depending upon the value of l

Value of l	0	1	2	3	. . .
Sublevel	s	p	d	f	. . .

Magnetic Quantum Number (m)

It refers to the *different orientations of the orbitals* in space. For a given value of l, m can have $(2l + 1)$ values as

$$m = +1, \ldots (l - 1) \ldots 0 \ldots -(l - 1) \ldots -1$$

Spin Quantum Number

This is designated by s and describes the spin orientation of the electron. Since the electron can spin only in two ways—clockwise and anticlockwise, s can have only two values: $+\frac{1}{2}$ and $-\frac{1}{2}$, which are also expressed by arrows pointing up (↑) and down (↓), respectively. It determines the orientation of spin angular momentum.

16.18 PROBABILITY DISTRIBUTION OF ELECTRONS IN AN ORBITAL

There are various ways of depicting the probability distribution of electrons in an orbital. One of the simplest is to show the variation of ψ, as a function of distance from the nucleus (r), for fixed θ and ϕ. Such a variation is known as *radial dependance* (Fig. 16.5). However, ψ has negative values (Fig. 16.5b) and shows both maxima and minima. It is therefore preferable to plot $|\psi^2|$ as a function of r(drawn on the same figure). This gives the *probability density* of finding the electron at different points in space.

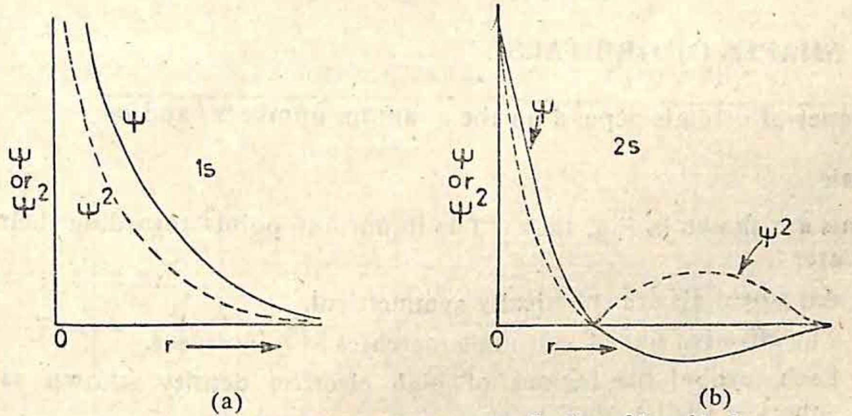


FIG. 16.5 *Plot of ψ and ψ^2 versus r for 1s and 2s orbital*

However, a more informative plot should give the total probability of finding the electron between r and $r + dr$ instead of just at a point. The volume of such a shell of extremely small thickness, dr, is $4\pi r^2 dr$. The function $4\pi r^2 \psi^2$ is called the *radial distribution function* and is plotted versus r (Fig 16.6). This takes into account ψ^2 and the volume of the shell. In the $1s$ orbital, it is zero at $r = 0$ (because volume of shell is zero), keeps increasing gradually, and reaches a maximum value (called the most probable value) and then decreases. For the hydrogen atom, the maximum value occurs at 0.529Å, which is the radius of the first orbit in Bohr's model.

The next higher orbital, $2s$, has two maxima and a zero probability region in between.

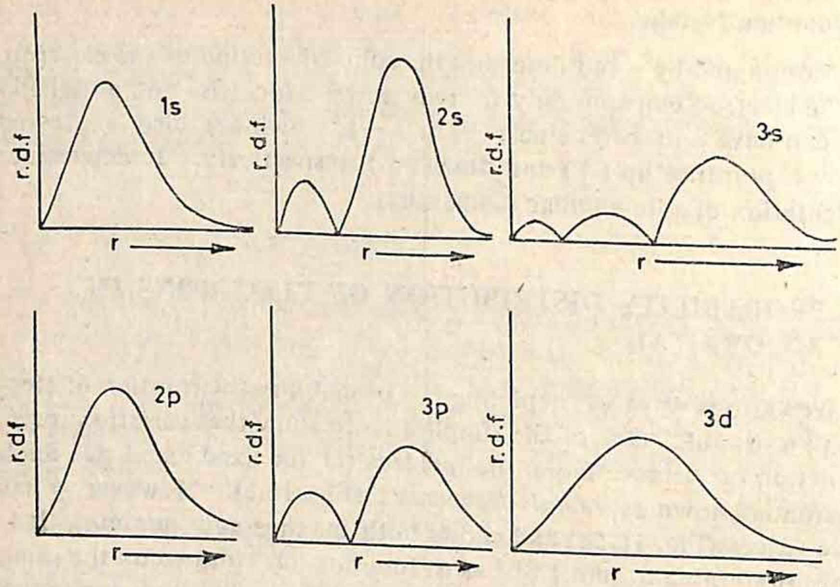


FIG. 16.6 *Radial probability distribution functions,* $4\pi r^2\psi^2$
(curves are not to the scale)

16.19 SHAPES OF ORBITALS

The shapes of orbitals depend on the quantum numbers *l* and *m*.

s-orbitals

s-orbitals are shown in Fig. 16.7. The important points regarding their shapes are:

1. All *s*-orbitals are spherically symmetrical.
2. The effective size of *s*-orbitals increases as *n* increases.
3. Each orbital has regions of high electron density (shown as spherical shells) equal to *n*.
4. In between the spherical shells there are nodes (having zero probability) equal to $n - 1$.

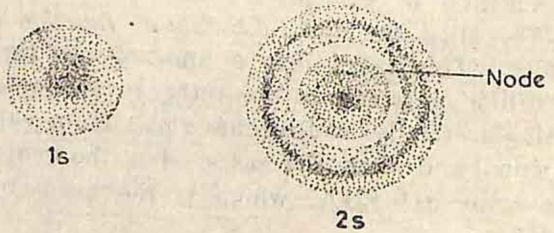


FIG. 16.7 *Shapes of 1s and 2s orbitals*

p-orbitals

There are three *p*-orbitals, designated as p_x, p_y and p_z, which are oriented along the three mutually perpendicular axes x, y and z. Each orbital consists of two lobes symmetrical about a particular axis and has *dumb bell* shape. The two lobes are separated by a nodal plane. Higher *p*-orbitals have similar shapes except that they have additional smaller regions of high electron density (called lobes) separated from the major lobes by the nodal surface. The number of such regions is $(n - 2)$ on each side.

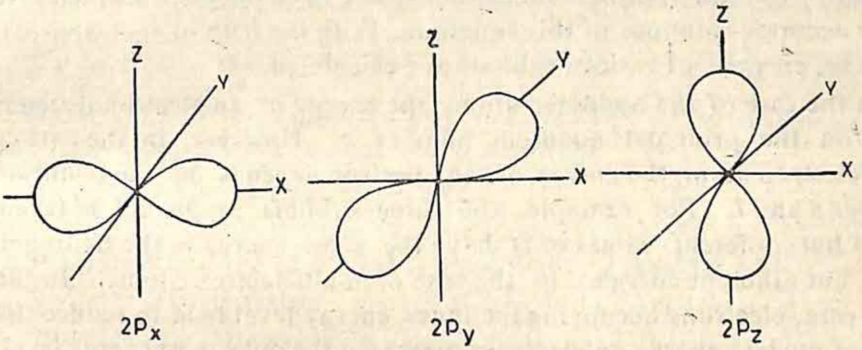


FIG. 16.8 *Shapes of 2p-orbitals.*

d-orbitals

There are five *d*-orbitals designated as d_{xy}, d_{yz}, d_{zx}, $d_{x^2-y^2}$ and d_{z^2}. These are shown in Fig. 16.9.

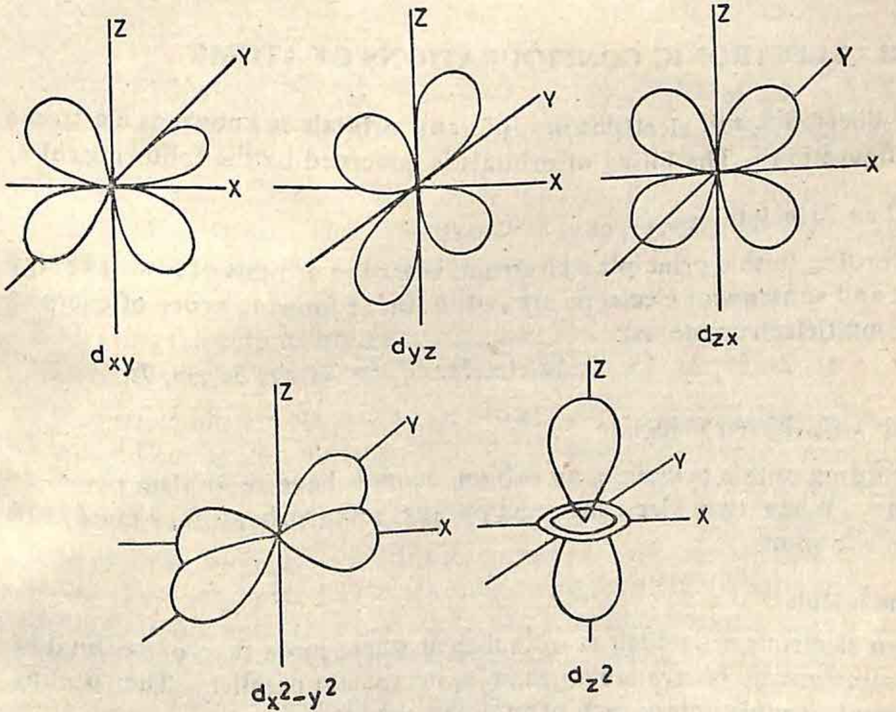


FIG. 16.9 *Shapes of 3d-orbitals*

f-orbitals

There are seven *f*-orbitals designated as $fx(x^2 - y^2)$, $fy(x^2 - y^2)$, $fz(x^2 - y)^2$ $fxyz$, fz^3, fyz^2 and fxz^2. Their shapes are complicated and are not discussed here.

16.20 MULTI-ELECTRON ATOMS

Solutions of the Schrödinger wave equation for multielectron atoms are difficult. Certain approximate methods have been developed which give fairly accurate solutions of this equation. With the help of such approximations, energies of various orbitals are calculated.

In the case of the hydrogen atom, the energy of an electron depends only on the principal quantum number *n*. However, in the case of multielectron atom, the energy of an electron depends on the quantum number *n* and *l*. For example, the three orbitals 3*s*, 3*p* and 3*d* (same $n = 3$ but different values of *l*) have the same energy in the hydrogen atom, but different energies in the case of multielectron atoms. In the latter case, electrons occupying the inner energy level tend to reduce the effect of nuclear charge on electrons present in the outermost energy level. In other words, electrons present in the inner energy levels screen or shield the outermost electrons from the nucleus (screening or shielding effect). This is different in different types of orbitals. Therefore, the orbitals *s*, *p*, *d*, *f*, . . . are screened differently and have different energies.

16 21 ELECTRONIC CONFIGURATIONS OF ATOMS

The distribution of electrons in different orbitals is known as electronic configuration. The filling of orbitals is governed by the following rules.

Aufbau Principle

According to this principle, electrons enter the orbitals of lowest energy first and subsequent electrons are fed in the following order of energies (for multielectron atoms):

1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*.

Pauli's Exclusion Principle

According to this principle, an orbital cannot have more than two electrons. When two electrons occupy the same orbital, they must have opposite spins.

Hund's Rule

When electrons are added to a subshell where more than one orbital of the same energy is available, their spins remain parallel. They occupy different orbitals unless each orbital has one electron.

Based upon the above rules and sequence of energy levels, electron configurations of various atoms can be written.

H(Z = 1) : $1s^1$ He(Z = 2) : $1s^2$

Li (Z = 3) : $1s^2 2s^1$ Be(Z = 4) : $1s^2 2s^2$

B (Z = 5) : $1s^2 2s^2 2p_x^1$ C(Z = 6) : $1s^2 2s^2 2p_x^1 2p_y^1$

(Hund's rule)

N(Z = 7) : $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ O(Z = 8) : $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$

F(Z = 9) : $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$ Ne(Z = 10) : $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

Similarly from sodium (Z = 11) to argon (Z = 18). However, for simplicity, a convention is used, e.g. for sodium:

Na(Z = 11) : $1s^2 2s^2 2p^6 3s^1$ or [Ne] $3s^1$

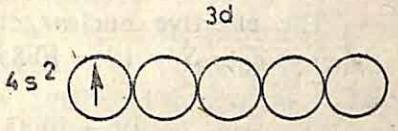
where [Ne] represents the inner core of neon ($1s^2 2s^2 2p^6$).

For potassium, the 4*s* orbital is filled first and then 3*d*, as:

K(Z = 19) : [Ar] $4s^1$ Ca(Z = 20) : [Ar] $4s^2$

From scandium onwards, the 3*d* subshell comes into use:

Sc(Z = 21) : [Ar] $4s^2\ 3d^1$ or [Ar]



Ti(Z = 22) : [Ar] $4s^2\ 3d^2$ or [Ar]

and so on.

However, it may be noted that there are two important irregularities in the general trend. The electronic configurations of chromium (Z = 24) and copper (Z = 29) are expected to be

Cr : [Ar] $4s^2 3d^4$ and Cu : [Ar] $4s^2 3d^9$

However, the actual configurations are:

Cr : [Ar]$4s^1 3d^5$ and Cu : [Ar] $4s^1 3d^{10}$

These irregularities are attributed to the fact that half-filled and completely filled configurations (e.g., d^5, d^{10}, f^7 and f^{14}) possess extra stability, one of the 4*s* electron goes to the 3*d* orbital so that 3*d* orbitals get half-filled or completely filled configurations in Cr and Cu, respectively.

The electron configurations of other atoms can be written in a similar fashion. For example, let us try thalium (Z = 81). The noble gas preceding atomic number 81, is Xe^{54}. The orbitals which follow this are 6*s*, 4*f*, 5*d*, 6*p*, . . . (from energy sequence). Thus,

Tl(Z = 81) : [Xe] $6s^2 4f^{14} 5d^{10}\ 6p^1$

16.22 EFFECTIVE NUCLEAR CHARGE—SLATER RULES

Due to screening by inner electrons, the outermost electron does not feel the complete charge of the nucleus. The actual charge experienced by an electron is called the *effective nuclear charge* (Z_{eff}). This is represented as Z_{eff} = Total nuclear charge (Z) − Screening constant (S). Slater proposed the following rules for determining the screening constant and effective nuclear charge.

1. Electrons farther away from the nucleus than the electron under consideration do not contribute to the screening constant S.

2. The electrons in the same group, *ns*, *np*, *nd* or *nf*, contribute $S = 0.35$ each (except 1*s* where 0.30 is used).

3. In the case *ns* and *np* groups, all electrons in the $(n - 1)$ shell contribute $S = 0.85$ each, and all electrons in the $(n - 2)$ shell contribute $S = 1$ each.

4. In the case of *nd* or *nf* orbitals, all electrons in lower groups contribute $S = 1$ each.

These rules are illustrated below:

(a) Potassium ($Z = 19$) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

The effective nuclear charge experienced by the 4*s* electron is

$$\begin{aligned} Z_{\text{eff}} = Z - S &= 19 - [0.85 \times (\text{number of electrons in } n = 3) + 1 \\ &\qquad \times (\text{number of electrons in } n < 3)] \\ &= 19 - [0.85 \times 8 + 1 \times 10] \\ &= 19 - 16.8 = 2.2 \end{aligned}$$

(b) Iron ($Z = 26$) : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^6\ 4s^2$

The effective nuclear charge experienced by 3*d* electrons is

$$\begin{aligned} Z_{\text{eff}} = Z - S &= 26 - [0.35 \times (\text{number of electrons in } 3d) \\ &\qquad + 1\ (\text{number of electrons in lower orbitals})] \\ &= 26 - [0.35 \times 5 + 1 \times 18] \\ &= 26 - 19.75 = 6.25 \end{aligned}$$

16.23 ATOMIC TERM SYMBOLS AND RUSSEL–SAUNDERS COUPLING

In an atom, an electron may have a spin angular momentum and an orbital angular momentum which may interact or couple to give a resultant angular momentum. The resultant angular momentum and energy of the system is expressed in a *term symbol*. The term symbol for a particular atomic state is denoted as ${}^{2S+1}L_J$ where S denotes the total spin quantum number and $2S + 1$ gives the *multiplicity* of the state, L is the total orbital angular quantum number and J gives the total angular quantum number. Like the symbols *s*, *p*, *d*, *f*, . . . for $l = 0, 1, 2, 3, \ldots$, the different values of L are designated as $L = 1$ (S), $L = 1$ (P), $L = 2$ (D), $L = 3$ (F), etc. These quantities are determined as given ahead.

(a) When two electrons interact with each other, the total spin S will be

$S = \frac{1}{2} + \frac{1}{2}$, or $\frac{1}{2} - \frac{1}{2}$, or $-\frac{1}{2} - \frac{1}{2}$, i.e. 1, 0 or -1

(b) When two electrons with azimuthal quantum number l_1, and l_2 interact, L can have the values:

$L = l_1 + l_2, l_1 + l_2 - 1, \ldots, | l_1 - l_2 |$

where the modulus sign || indicates that the positive value, $l_1 - l_2$ or $l_2 - l_1$, is to be taken.

(c) The L and S values couple to give a series of J values for all electrons.

$J = L + S, L + S - 1, L + S - 2, \ldots, | L - S |$

This interaction is called *Russell–Saunders coupling*.

Coupling

(d) For a three-electron system, L is calculated by calculating L_1 values for two electrons, which are then combined with the third value of l to get the resultant L values. S can also be determined as

$S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2}, \frac{1}{2} + \frac{1}{2} - \frac{1}{2}$ etc. i.e. 3/2 and $\frac{1}{2}$.

(e) In general, multiplicity is $2S + 1$, except when $L < S$. In this case only one value of J is obtained.

It may be noted that L–S coupling is applicable for atoms of light atomic mass. For atoms of heavy mass, J-J coupling occurs. In this case the l_i and s_i of each electron is combined to give the j values. Individual j values interact to give the total J for the atom.

EXAMPLE 16.13 Write the term symbols for boron ($1s^2\,2s^2\,2p^1$) and carbon ($1s^2\,2s^2\,2p^2$) atoms.

Solution For closed and filled shells, $L = 0$ and $S = 0$. The L and S values will be determined by $2p$ electrons only.

For this, $l = 1$, so that $L = 1$

$S = \frac{1}{2}$ so that $2S + 1 = 2$

$J = L + S, L + S - 1, \ldots, | L - S |$

$= \frac{3}{2}, \frac{1}{2}$

Term symbols for boron $= 2P_{3/2}, 2P_{1/2}$

For carbon : $1s^2\,2s^2\,2p^2$

For both p electrons, $l = 1$, so that

$L = 1 + 1,\ 1 + 1 - 1,\ 1 - 1 = 2, 1, 0$

The corresponding symbols are D, P and S

$S = \frac{1}{2} + \frac{1}{2}$ or $\frac{1}{2} - \frac{1}{2}$, i.e. 1, 0

Spin multiplicity = 3, 1

Now $J = L + S,\ L + S - 1, \ldots, | L - S |$

For $L = 2,\ S = 1,\ J = 2 + 1,\ 2 + 1 - 1,\ 2 - 1 = 3, 2, 1$

For $L = 2,\ S = 0,\ J = 2$

For $L = 1,\ S = 1$ and $J = 0$

For $L = 1,\ S = 0$ and $J = 1$

For $L = 0$, $S = 1$ and $J = 1$
$L = 0$, $S = 0$ and $J = 0$

J can have values 3, 2, 1 or 0.

Thus, term symbols are
${}^3D_3$, ${}^3D_2$, ${}^3D_1$, ${}^1D_2$, ${}^3P_0$, ${}^1P_1$, ${}^3S_1$, ${}^1S_0$

MISCELLANEOUS EXAMPLES

EXAMPLE 16.14 In the spectrum of the hydrogen atom, a spectral line corresponds to transition from a fifth orbit to the second orbit.

(a) Calculate the frequency and wavelength of this radiation.

(b) To which spectral series does this line belong and in what region of the electromagnetic spectrum will this line fall?

(c) Calculate the highest frequency corresponding to this spectral series (Rydberg constant = 3.289×10^{15} s^{-1}).

Solution (a) The frequency of the spectral line emitted in the case of the hydrogen atom when an electron jumps from n_2 to n_1 level is given by

$$\nu = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 3.289 \times 10^{15}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \text{s}^{-1}$$

$$n_2 = 5,\ n_1 = 2$$

$$\nu = 3.289 \times 10^{15}\left(\frac{1}{4} - \frac{1}{25}\right)$$
$$= 6.9 \times 10^{14} \text{ s}^{-1}$$

Now, wavelength $\lambda = \frac{c}{\nu}$ where $c = 3 \times 10^8$ m s^{-1}

$$= \frac{3 \times 10^8 \text{ m s}^{-1}}{6.9 \times 10^{14} \text{ s}^{-1}} = 4.348 \times 10^{-7} \text{ m}$$
$$= 4348 \text{ Å}$$

(b) The line corresponds to the jump from $n = 5$ to $n = 2$. It belongs to the Balmer series and will fall in the visible region.

(c) The line having the highest frequency will correspond to the highest energy. Thus, the transition will be from the highest level, $n_2 = \infty$ to $n_1 = 2$

$$\therefore \quad \nu = 3.289 \times 10^{15}\left(\frac{1}{2^2} - \frac{1}{\infty}\right)$$
$$= \frac{3.289 \times 10^{15}}{4} = 8.22 \times 10^{14} \text{ s}^{-1}$$

EXAMPLE 16.15 Calculate the frequencies and wavelengths of spectral lines emitted in the case of the hydrogen atom or He$^+$ ion when an electron in each case jumps from the third to the first orbit (Rydberg constant = 3.29×10^{15} s^{-1}).

Solution The frequency of the spectral line in the case of the H atom,

$$\nu = 3.29 \times 10^{15} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$n_1 = 1,\ n_2 = 3$$

$$\therefore \quad \nu = 3.29 \times 10^{15} \left(\frac{1}{1^2} - \frac{1}{3^2} \right)$$

$$= 2.92 \times 10^{15}\ \text{s}^{-1}$$

Now, wavelength $\lambda = \dfrac{c}{\nu}$

$$= \frac{3 \times 10^8\ \text{m s}^{-1}}{2.92 \times 10^{-15}\ \text{s}^{-1}}$$

$$= 1.027 \times 10^{-7}\ \text{m} = 1027\ \text{Å}$$

In case of He$^+$,

$$\nu = 3.29 \times 10^{15}\, Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$Z = 2,\ n_1 = 1,\ n_2 = 3$$

$$\nu = 3.29 \times 10^{15} \times (2)^2 \left(\frac{1}{1^2} - \frac{1}{3^2} \right)$$

$$= 11.70 \times 10^{15}\ \text{s}^{-1}$$

and wavelength $\lambda = \dfrac{c}{\nu}$

$$= \frac{3 \times 10^8\ \text{m s}^{-1}}{11.70 \times 10^{15}\ \text{s}^{-1}}$$

$$= 2.56 \times 10^{-8}\ \text{m} = 256\ \text{Å}$$

QUESTIONS

Numerical Problems

16.1 (SI Units) Calculate the frequency and the energy of a photon associated with light of wavelength 450 nm.

16.2 (SI Units) Calculate the wavelength and wave number associated with a radiation having frequency $2 \times 10^{12}\ \text{s}^{-1}$.

16.3 Which of the following radiations has the highest energy

(a) Radiation of frequency $= 3 \times 10^{15}\ \text{s}^{-1}$
(b) Radiation of wavelength $= 400$ nm
(c) Radiation of wave number $= 2.8 \times 10^8\ \text{cm}^{-1}$

16.4 (SI Units) The energy difference between two electronic states of hydrogen atom is 207.9 kJ mol^{-1}. Calculate the frequency and wavelength of light emitted when an electron drops from higher energy level to lower energy level ($h = 3.98 \times 10^{-13}$ kJ s mol^{-1}).

16.5 The threshold energy for photoelectric emission of electrons from a metal is 3.124×10^{-19} J. If light of 450 nm wavelength is used, will the electrons be ejected or not ?

16.6 If light with wavelength 400 nm falls on the surface of sodium metal, electrons with velocity 5.41×10^5 m s^{-1} are ejected.
  (a) Calculate the minimum frequency and the corresponding wavelength of light required to eject an electron from sodium metal.
  (b) What is the value of work function in eV ?
  $(1\ \text{J} = 6.25 \times 10^{18}\ \text{eV})$

16.7 The threshold frequency for photoelectric emission of cesium is 4.55×10^{14} s^{-1}. Calculate the kinetic energy in (a) J (b) eV of a photoelectron produced in cesium by light of wavelength 400 nm.

16.8 Calculate the radius and velocity of the electron in the third Bohr orbit for hydrogen atom and He$^+$.

16.9 Calculate the frequency and wavelength associated with the transition from $n = 4$ to $n = 1$ level in hydrogen atom.

16.10 Find out the electronic state from which an electron jumps to emit rediation with wavelength 1212 Å and gives a line in the Lyman series of the hydrogen spectrum (Rydberg constant = 109678 cm^{-1}).

16.11 Calculate the frequency of the first and limiting line in the Balmer series.

16.12 An electromagnetic radiation of wavelength 245 nm is just sufficient to ionise the outermost electron of the sodium atom. Calculate the ionisation energy of sodium atom.

16.13 Calculate
  (a) the radius of the fourth Bohr orbit of hydrogen atom
  (b) the energy of the electron in this orbit

16.14 Calculate the wavelength and frequencies of spectral lines emitted in case of the hydrogen atom and He$^+$ ion, when the solitary electron jumps from the second to the first orbit in each case.

16.15 (SI Units) Calculate the wavelength of a proton (mass = 1.673×10^{-27}) when it is accelerated through a potential difference of 2×10^6 V.

16.16 (SI Units) A particle associated with a wavelength of 6.6 nm is moving with a velocity of 1×10^6 m s^{-1}. Calculate the mass of the particle.

16.17 Calculate the uncertainty in position of an electron when its momentum is to be measured with an accuracy of 1%.

16.18 The uncertainties in velocity and position of a particle are 1.17×10^{10} cm s^{-1} and 1×10^{-2} Å, respectively. Calculate the minimum mass of the particle.

16.19 The ground state electronic configuration of potassium may be (a) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 4s^1$ or (b) $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^1$. Calculate the effective nuclear charge felt by the 4*s* electron in configuration (a) and 3*d* electron in configuration (b). Which configuration is correct.

16.20 Calculate the effective nuclear charge on a 3*d* and a 4*s* electron in vanadium: $1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^3\, 4s^2$.

QUIZ QUESTIONS

Type A: Multiple Choice

16.21 Which of the following statements is wrong regarding cathode rays ?
  (a) The rays produce a mechanical effect.
  (b) The charge/mass ratio is independent of the nature of the gas taken in the discharge tube.
  (c) The charge/mass ratio for these rays is considerably smaller than for positive rays.
  (d) The rays carry a negative charge.

16.22 Rutherford observed that only a few (about one in a million) α-particles were deflected back on bombarding a piece of gold foil. Most of the α-particles which were not deflected back

(a) caused the gold to become radioactive
(b) were absorbed by the gold foil
(c) passed through the extranuclear part of the atom
(d) were neutralised by the negative electrons

16.23 Which of the following statements is not correct with regard to Rutherford's nuclear model of an atom?
(a) An atom consists of a nucleus surrounded by electrons revolving around it
(b) The nucleus is extremely small as compared to the atom
(c) The number of protons and neutrons in the nucleus of an atom are always equal
(d) Most of the atom is empty space.

16.24 Which of the following relations between wave number ($\bar{\nu}$), frequency (ν) and speed (c) is correct?
(a) $\nu = c \times \frac{1}{\nu}$ (b) $c/\bar{\nu} = \bar{\nu}$
(c) $\nu = c \times \nu$ (d) $\bar{\nu} = \nu \times c$

16.25 Which is the correct order of wave number of the following radiations: infrared, ultraviolet, radio waves, x-rays and visible light.
(a) x-rays > ultraviolet > infrared > visible > radio waves
(b) x-rays > ultraviolet > visible > infrared > radio waves
(c) radio waves > infrared > visible > ultraviolet > x-rays
(d) x-rays > radio waves > visible > ultraviolet > infrared

16.26 Which of the following statements is not correct regarding the electromagnetic spectra ?
(a) Cosmic rays have shorter wavelengths than radio waves.
(b) X-rays have smaller wave number than cosmic rays.
(c) The velocity of x-rays is more than that of microwaves.
(d) The frequency of microwaves is less than that of ultraviolet rays.

16.27 According to Bohr's model of an atom, the electrons rotate around the nucleus in
(a) orbitals (b) subshells
(c) orbits (d) charge clouds

16.28 Which of the following observations is false about the photoelectric effect:
(a) The kinetic energy of photoelectrons depends upon the frequency of the incident radiation
(b) The number of photoelectrons ejected from the metal surface depends upon the intensity of the incident radiation
(c) The threshold frequency is the same for all metals
(d) The kinetic energy of ejected electrons is independent of the intensity of radiation.

16.29 The correct expression derived by Bohr for the energy of an electron in the *n*th energy level of hydrogen, is (esu)
(a) $E_n = \frac{2\pi^2 me^4}{n^2h^2}$ (b) $E_n = -\frac{2\pi^2 me^4}{nh^2}$
(c) $E_n = -\frac{2\pi^2 me^2}{h^2}$ (d) $E_n = -\frac{2\pi^2 me^4}{n^2h^2}$

16.30 Which of the following transitions of electrons in the hydrogen atom will emit maximum energy ?
$n_5 \to n_4;\ n_4 \to n_3;\ n_3 \to n_2$
(a) $n_5 \to n_4$ (b) $n_4 \to n_3$
(c) $n_3 \to n_2$ (d) same in all transitions

16.31 The radius of the *n*th Bohr orbit is given by

(a) $\frac{2\pi^2 me^4}{n^2h^2}$ (b) $\frac{n^2h^2}{4\pi^2 me^2}$

(c) $\frac{nh}{2\pi e^2}$ (d) $\frac{2\pi e^2}{nh}$

16.32 The radii of different Bohr orbits (n) can be obtained from the relation

(a) $0.53\ n^2$ nm (b) $0.053\ n^2$ nm

(c) $\frac{0.053}{n^2}$ nm (d) $0.53\ n$ nm

16.33 If λ_0 is the threshold wavelength for photoelectric emission, λ the wavelength of light falling on the surface of a metal and m the mass of an electron, then, the velocity of the ejected electron is given by

(a) $\left[\frac{2h}{m}(\lambda_0-\lambda)\right]^{\frac{1}{2}}$

(b) $\left[\frac{2hc}{m}(\lambda_0-\lambda)\right]^{\frac{1}{2}}$

(c) $\left[\frac{2hc}{m}\left(\frac{\lambda_0-\lambda}{\lambda_0\lambda}\right)\right]^{\frac{1}{2}}$

(d) $\left[\frac{2h}{m}\left(\frac{1}{\lambda_0}-\frac{1}{\lambda}\right)\right]^{\frac{1}{2}}$

16.34 The spectral line obtained when an electron jumps from $n = 6$ to $n = 2$ belongs to the

(a) Balmer series (b) Lyman series

(c) Paschen series (d) Pfund series

16.35 The wave character of an electron was experimentally verified by

(a) Einstein (b) de Broglie

(c) Germer (d) Planck

16.36 The de Broglie relationship can be expressed as

(a) $h = \frac{\lambda}{mv}$ (b) $\lambda = \frac{h}{mp}$

(c) $\lambda m = \frac{v}{h}$ (d) $\lambda = \frac{h}{mv}$

16.37 Heisenberg's uncertainty principle precludes the exact simultaneous measurement of

(a) charge density and probability

(b) position and momentum

(c) position and direction

(d) velocity and energy

16.38 The correct Schrödinger wave equation for an electron, in a potential field V, in three dimensions is (where the symbols have their usual meanings)

(a) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2}{mh^2}(E-V)\psi=0$

(b) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h}(E-V)\psi=0$

(c) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E-V)\psi=0$

(d) $\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}+\frac{8\pi^2 m}{h^2}(E+V)\psi=0$

16.39 Which of the following conditions is incorrect for well-behaved wave function (ψ) ?

(a) ψ must be finite.
(b) ψ must be single valued at any particular point.
(c) ψ must be positive.
(d) ψ must be a continuous function of its coordinates.

16.40 The first main energy shell that can have f orbitals is the
(a) first
(b) second
(c) third
(d) fourth

16.41 For $n = 3$, which value of l is not possible ?
(a) 0
(b) 1
(c) 2
(d) 3

16.42 For each value of l, the number of m values are
(a) $2l$
(b) n^2
(c) $(2l + 1)$
(d) $(n + 1)$

16.43 The maximum number of electrons in first energy level are
(a) 1
(b) 2
(c) 8
(d) 18

16.44 For $l = 3$, which value of m is not possible ?
(a) 0
(b) -3
(c) 4
(d) -1

16.45 The possible sublevels in the $n = 4$ energy level are
(a) s, p, d
(b) s, p, d, f
(c) s
(d) s, p, d, f, g

16.46 If the principal quantum number $n = 4$, the quantum number l can have the values
(a) 1, 2, 3 and 4
(b) 0, 1, 2 and 3
(c) 1, 2 and 3 only
(d) $0, \pm 1, \pm 2$ and ± 3

16.47 The designation of an orbital with $n = 4$ and $l = 1$ is
(a) $4s$
(b) $4p$
(c) $4d$
(d) $4f$

16.48 The maximum number of electrons in the third main energy level, $2p_y$ orbital and $3d$ subshell are
(a) 9, 6, 10
(b) 18, 6, 10
(c) 9, 2, 5
(d) 18, 2, 10

16.49 Which of the following orbitals does not make sense ?
(a) $6f$
(b) $7s$
(c) $2d$
(d) $5g$

16.50 Which of the following sets of quantum numbers is possible for an electron in a $4f$ orbital ?
(a) $n = 4 \; l = 3 \; m = 4 \; s = +\frac{1}{2}$
(b) $n = 4 \; l = 4 \; m = +4 \; s = +\frac{1}{2}$
(c) $n = 4 \; l = 3 \; m = +1 \; s = -\frac{1}{2}$
(d) $n = 4 \; l = 2 \; m = 2 \; s = +\frac{1}{2}$

16.51 The maximum number of $4f$ electrons having spin quantum nnmber $s = -\frac{1}{2}$ are
(a) 14
(b) 7
(c) only one
(d) any number from 1 to 14

16.52 The maximum number of electrons in the s, p, d and f subshells are
(a) 2 in each
(b) 2, 6, 10, 14
(c) 2, 6, 8, 10
(d) 2, 3, 5, 7

16.53 Which of the following sets of quantum numbers is possible?
(a) $n = 4$ $l = 3$ $m = -3$ $s = 0$
(b) $n = 4$ $l = 0$ $m = 0$ $s = +\frac{1}{2}$
(c) $n = 4$ $l = 4$ $m = -4$ $s = -\frac{1}{2}$
(d) $n = 4$ $l = 0$ $m = +2$ $s = -\frac{1}{2}$

16.54 The number of orbitals in $n = 4$ are
(a) 2
(b) 8
(c) 16
(d) 32

16.55 The maximum number of electrons in an atom with $l = 2$ and $n = 3$ is
(a) 2
(b) 6
(c) 10
(d) 12

16.56 The total number of maxima in the radial probability distribution curve of $4d$ are
(a) two
(b) three
(c) four
(d) six

16.57 The orbitals $3s$, $3p$, $5s$, $6s$, $4p$ and $4f$ can be arranged in the following order of increasing energy for the hydrogen atom
(a) $3s < 3p < 4p < 4f < 5s < 6s$
(b) $3s < 3p < 4p < 5s < 4f < 6s$
(c) $3s = 3p < 4p = 5s < 4f < 6s$
(d) $3s = 3p < 4p = 4f < 5s < 6s$

16.58 The electronic configuration of chromium ($Z = 24$) in the ground state is
(a) $[Ar]\,4s^2\,3d^4$
(b) $[Ar]\,3d^6$
(c) $[Ar]\,4s^1\,3d^5$
(d) $[Ar]\,4s^2\,3d^6$

16.59 Which is the correct configuration of Fe^{3+} ($Z = 26$)?
(a) $[Ar]\,4s^2\,3d^6$
(b) $[Ar]\,3d^5$
(c) $[Ar]\,4s^2\,3d^3$
(d) $[Ar]\,4s^2\,3d^4$

16.60 Which of the following term symbols is not correct for a state corresponding to $L = 2$, $S = 1$?
(a) $3P_1$
(b) $3D_3$
(c) $3D_2$
(d) $3D_1$

Type B: Multiple Choice (Numerical Problems)

16.61 The frequency of a wave is 90×10^6 Hz. Its wavelength is equal to
(a) 3×10^{-5} m
(b) 3.3×10^2 m
(c) 3.3 m
(d) 3×10^{-3} m

16.62 The wavelength of green light is 500 nm. Its frequency is equal to
(a) 6×10^{14} Hz
(b) 6 Hz
(c) 1.5×10^2 Hz
(d) 1.5 Hz

16.63 The wavelength of blue light is 4000 Å. Its frequency and wave number are
(a) $7.50 \times 10^{14}\ s^{-1}$ and $2.5 \times 10^{-4}\ cm^{-1}$
(b) $15 \times 10^{14}\ s^{-1}$ and $2.5 \times 10^{-6}\ m^{-1}$
(c) $7.50 \times 10^{14}\ s^{-1}$ and $2.5 \times 10^{6}\ m^{-1}$
(d) $7.50 \times 10^{-14}\ s^{-1}$ and $2.5 \times 10^{4}\ cm^{-1}$

16.64 The wavelength of the light emitted by a certain source is 500 nm. The wave number of this light is
(a) 5×10^{-7} m
(b) 2×10^{6} m
(c) 0.2×10^{-9} m
(d) 2×10^{8} m

16.65 The energy of the photon of wavelength 4500 Å is
(a) 4.4×10^{-19} J

(b) 4.4×10^{-20} J
(c) 4.4×10^{-12} J
(d) 0.4×10^{-6} J

16.66 An atom emits energy equal to 4×10^{-12} erg. In which part of the electromagnetic spectrum does the corresponding line lie ?
(a) ultraviolet region
(b) infrared region
(c) visible region
(d) microwave region

16.67 The threshhold frequency for a metal is 4×10^{14} s^{-1}. The minimum energy which the photons must possess to produce a photoelectric effect with the metal is ($h = 6.6 \times 10^{-34}$ J)
(a) 3.06×10^{-12} J
(b) 1.4×10^{-48} J
(c) 3.4×10^{-19} J
(d) 2.64×10^{-19} J

16.68 An atom absorbs 3.0×10^{-19} J of energy. In the spectrum of this atom, where would there be a missing wavelength corresponding to this energy?
(a) 6.6×10^{-7} m
(b) 2.21×10^{-15} m
(c) 6600 m
(d) 2.21×10^{-5} m

16.69 The frequency of light emitted when an electron jumps from a higher energy level n_2 to the lower energy level n_1 is

$$\nu = 3.29 \times 10^{15}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

The limiting line in the Balmer series will have a frequency equal to
(a) 3.29×10^{15} s^{-1}
(b) -3.65×10^{14} s^{-1}
(c) -8.22×10^{14} s^{-1}
(d) 8.22×10^{14} s^{-1}

16.70 The energy of the second Bohr orbit of the hydrogen atom is -3.41 eV. The energy of the second Bohr orbit of the He$^+$ ion will be
(a) -6.82 eV (b) -13.62 eV
(c) -1.70 eV (d) -0.85 eV

16.71 The energy of the *n*th Bohr orbit of the hydrogen atom is given by the relation

$$E_n = -\frac{2.18 \times 10^{-18}\text{J}}{n^2}$$

The frequency of the light emitted when an electron jumps from the third to the first orbit is ($h = 6.6 \times 10^{-34}$ J s)
(a) 1.65×10^{15} s^{-1}
(b) 1.65×10^{16} s^{-1}
(c) 1.65×10^{17} s^{-1}
(d) 1.65×10^{10} s^{-1}

16.72 The threshold wavelength for the ejection of electron from metal *X* is 330 nm. The work function for photoelectric emission from metal *X* is ($h = 6.6 \times 10^{-34}$J s)
(a) 1.2×10^{-18} J
(b) 1.2×10^{-20} J

(c) 6×10^{-19} J
(d) 6×10^{-12} J

16.73 The de Broglie wavelength of an electron is 66 nm. The velocity of the electron is ($h = 6.6 \times 10^{-34}$ J s, mass of electron $= 9 \times 10^{-31}$ kg) ?
(a) 1.1×10^{3} m s^{-1}
(b) 1.1×10^{4} m s^{-1}
(c) 5.4×10^{8} m s^{-1}
(d) 1.84×10^{-4} m s^{-1}

16.74 The uncertainty in the momentum of an electron is 1×10^{-9} kg m s^{-1}. The uncertainty in position will be ($h = 6.63 \times 10^{-34}$ kg m^2 s^{-1})
(a) 1.05×10^{-23} m
(b) 2.1×10^{-25} m
(c) 1.05×10^{-27} m
(d) 1.05×10^{-25} m

16.75 The effective nuclear charge experienced by a 4*d* electron of *Y*, having electronic configuration [Kr] $5s^2\ 4d^1$, is
(a) 1.00 (b) 3.30
(c) 4.65 (d) 3.45

Type C: True or False

16.76 The electron spin quantum number describes the orientation of the spin of the nucleus with respect to the magnetic field.
16.77 If the value of $l = 0$, the orbital is spherically symmetrical.
16.78 The maximum number of 2*p* electrons in an atom with the spin quantum number $+1/2$ is three.
16.79 The orbitals represented by the quantum numbers $n = 3, l = 2, m = +2$ and $n = 3, l = 2, m = -2$ have the same energy.
16.80 All photons possess the same amount of energy.
16.81 The wave function (ψ) gives the probability of finding the electron in space.
16.82 The probability of finding the electron along the x and y axes in the dz_2 orbital is zero.
16.83 An electron has a smaller wavelength than a rocket moving with the same velocity.
16.84 The energy of a photon is directly proportional to wavelength but inversely proportional to wave number.
16.85 The frequency of radio waves is smaller than that of x-rays.
16.86 Bohr's quantum condition is that the angular momentum of an electron is an integral multiple of π/h.
16.87 According to the uncertainty principle, the product of the uncertainty in position and momentum is always constant.
16.88 The wave character of the electron was verified by de Broglie.
16.89 The radial part of the wave function depends on quantum number *n* only.
16.90 In the photoelectric effect, the kinetic energy of ejected electrons increases with increase in wavelength of radiation.

Type D: Fill in the Blanks

16.91 The Paschen series arises when an electron jumps from higher energy levels to ———— energy level in a hydrogen atom.
16.92 The number of electrons having $l = 1$ and $n = 2$ are ————.
16.93 The wavelength of x-rays is of the order of ———— nm.
16.94 Lyman series appear in ———— region.
16.95 The number of nodes in 4*s* orbital is ———— .
16.96 For $l = 2$, the different values of *m* are ———— .

16.97 For $m = 0$, the different values of s are ———— .

16.98 Emission of electrons from certain metals, when exposed to light, is known as ———— effect.

16.99 If an electron orbital has a shape designated by $l = 2$, there are ———— possible orientations of this orbital in space.

16.100 Discrete quantities of energy of light radiations are called ———— .

ANSWERS

Numerical Problems

16.1 (a) 0.75×10^{15} (b) 4.97×10^{-19} J *16.2* 1.5×10^{-4} m, 6.67×10^{3} m^{-1} *16.3* (a) 1.98×10^{-18} J (b) 4.96×10^{-19} J (c) 5.56×10^{-19} J *16.4* 574.7 nm *16.5* electrons will be ejected *16.6* (a) 5.49×10^{14} s^{-1}, 546.4 nm (b) 2.27 eV *16.7* 1.95×10^{-19} J, 1.21 eV *16.8* 4.77 Å, 7.26×10^{7} cm s^{-1} *16.9* 97.4 nm *16.10* 2 *16.11* 4.57×10^{14}, 8.225×10^{14} *16.12* 5.36 eV *16 13* (a) 8.48 Å (b) -82.0 kJ mol^{-1} *16.14* 1219 Å, 2.46×10^{15}; 304.8 Å, 9.84×10^{15} *16.15* 2.03×10^{-14} m *16.16* 1.004×10^{-31} kg *16.17* 1.05×10^{-6} cm *16.18* 9.01×10^{-28} g *16.19* 2.20, 1.0; (a) is correct *16.20* 4.30, 3.30.

Quiz Questions

16.21 (c) *16.22* (c) *16.23* (c) *16.24* (c) *16.25* (b) *16.26* (c) *16.27* (c) *16 28* (c) *16.29* (d) *16.30* (c) *16.31* (b) *16.32* (b) *16.33* (c) *16.34* (a) *16 35* (c) *16 36* (d) *16.37* (b) *16.38* (c) *16.39* (c) *16.40* (d) *16.41* (d) *16.42* (c) *16.43* (b) *16.44* (c) *16 45* (b) *16.46* (c) *16.47* (a) *16.48* (d) *16.49* (c) *16.50* (c) *16.51* (c) *16.52* (b) *16.53* (b) *16.54* (c) *16.55* (c) *16.56* (a) *16.57* (d) *16.58* (c) *16.59* (b) *16.60* (a) *16.61* (b) *16.62* (a) *16.63* (c) *16.64* (b) *16.65* (a) *16 66* (c) *16 67* (d) *16.68* (a) *16.69* (d) *16.70* (b) *16.71* (a) *16.72* (c) *16.73* (b) *16.74* (d) *16.75* (a) *16.76* False *16 77* True *16.78* False: One only *16.79* True *16.80* False: Energy of photon depends on frequency, $E = h\nu$ *16.81* False: ψ gives amplitude of the electron wave *16.82* False *16.83* False *16.84* False: Directly proportional to wave number and inversely proportional to wavelength ($E = h\nu = hc/\lambda = hc\bar{\nu}$ *16.85* True *16.86* False *16.87* True *16.88* False *16.89* False *16.90* False *16 91* third *16.92* six *16.93* 10 *16.94* ultraviolet *16.95* three *16.96* $+2, +1, 0, -1, -2$ *16.97* $+1/2$, $-1/2$ *16.98* Photoelectric effect *16.99* five *16.100* photons

17

Chemical Bonding

Atoms combine with one another in different ways and form a large variety of molecules. The attractive force which holds together the constituents in a chemical species is known as a chemical bond. The theory of chemical bonding is the central problem of modern chemistry. Without this knowledge, it would be difficult to understand the reasons for the existence of large variety of known compounds.

17.1 CAUSE OF CHEMICAL COMBINATION

It was observed that atoms of noble gases had little tendency to combine with one another or with atoms of other elements, because of the greater stability of their ns^2np^6 electronic configurations. In the case of other elements, atoms combine with each other or with atoms of other elements to acquire noble gas configurations. This tendency of atoms to attain a maximum of eight electrons in the valence shell was known as the *octet rule*. However, this rule could not be made universal because of the formation of compounds like PF_5, SF_6, BCl_3 where the central atom has more or less than eight electrons in the valence shell. Moreover, it has been found that even noble gases combine to form compounds like XeF_2, KrF_2, $XeOF_2$, XeO_3, etc.

According to the modern theory of chemical bonding, atoms form bonds because it leads to a decrease in energy. For example, when two hydrogen atoms approach each other, attractive and repulsive forces operate simultaneously. The attractive forces tend to bring two atoms close to each other and decrease the potential energy of the system, whereas the repulsive forces tend to push the atoms apart and increase the potential energy. It has been found that the magnitude of the attractive forces, in the case of two hydrogen atoms, is more than the repulsive forces and, therefore, potential energy decreases as the two atoms approach each other. Eventually, a state is reached (corresponding to a distance of 0.74 Å, called bond length) where the attractive forces balance the repulsive forces. At this stage, the potential energy of the system is minimum and the hydrogen atoms are said to be bonded to form a stable molecule. In case the repulsive forces dominate over the attractive forces, as when two helium atoms approach each other, the energy of the system increases and leads to instability. Consequently, a bond is not formed.

17.2 TYPES OF BONDS

Chemical bonds may be classified as
- (a) ionic bonds
- (b) covalent bonds
- (c) metallic bonds

In addition, attractive interactions between atoms of different molecules can give rise to weak bonds of the following types:
- (d) hydrogen bond
- (e) Van der Waal's interactions.

17.3 IONIC BOND

An ionic bond is formed by the complete transference of one or more valence electrons of one atom to the valence shell of the other. The oppositely charged ions thus formed are mainly held together by electrostatic forces of attraction. Because of the electrostatic nature of the binding force, the bond is also known as an *electrovalent bond* For example, the formation of sodium chloride takes place by the transference of one electron from the sodium to the chlorine atom, forming Na^+Cl^-.

$$\dot{Na} + \cdot\ddot{\underset{\cdot\cdot}{Cl}}: \longrightarrow Na^+\left[:\ddot{\underset{\cdot\cdot}{Cl}}:\right]^- \qquad \text{or} \quad Na^+Cl^-$$

17.4 LATTICE ENERGY OF IONIC CRYSTALS

The stability of ionic crystals is determined in terms of their lattice energy. This is defined as the amount of energy released when one mole of the ionic crystal is formed from its constituent ions in the gaseous phase,

$$M^+(g) + X^-(g) \longrightarrow MX(s);\ \Delta U = \text{Lattice energy} = -\Delta U_{\text{lattice}} \qquad (17.1)$$

The Born–Lande expression for lattice energy is

$$\Delta U_{\text{lattice}} = -\frac{N_A\, AZ_+Z_-e^2}{r_0}\left(1-\frac{1}{n}\right) \qquad (17\ 2)$$

where Z_+ and Z_- are the charges of positive and negative ions separated by distance r_0, e is the electronic charge, N_A is Avogadro's number, A is the Madelung constant and n is known as the Born exponent. The value of A depends only on the geometry of the crystal, n can be calculated from compressibility data and generally lies between 7 and 9.

17.5 BORN-HABER CYCLE

Born and Haber (1919) proposed a cycle, known as the Born-Haber cycle, to relate the lattice energy of an ionic compound to other thermochemical data. For example, for the formation of NaCl, the various steps may be represented as:

$$Na(s) + \tfrac{1}{2}\,Cl_2(g) \longrightarrow NaCl(s)$$

(1) Conversion of metallic sodium into gaseous sodium atoms

$$Na(s) \longrightarrow Na(g) \qquad \Delta U_{sub} = \text{Sublimation energy}$$

(2) Dissociation of chlorine molecules into chlorine atoms

$$\tfrac{1}{2}\,Cl_2(g) \longrightarrow Cl(g) \qquad \tfrac{1}{2}\,\Delta U_D = \text{Dissociation energy}$$

(3) Conversion of gaseous sodium atoms into sodium ions

$$Na(g) \longrightarrow Na^+(g) + e^-(g) \qquad \Delta U_{IE} = \text{Ionisation energy}$$

(4) Conversion of gaseous chlorine atoms into gaseous chloride ions

$$Cl(g) + e^- \longrightarrow Cl^-(g) \qquad \Delta U_{EA} = \text{Electron affinity}$$

(5) Formation of sodium chloride crystal lattice. The energy change in the process is the negative of the lattice energy.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s) \qquad \Delta U_{lattice} = \text{Lattice energy}$$

The overall energy change (ΔU) may be expressed as

$$\Delta U_f = \Delta U_{sub} + \tfrac{1}{2}\Delta U_D + \Delta U_{IE} + \Delta U_{EA} + \Delta U_{lattice}$$

Substituting the various values, lattice energy can be calculated. The Born-Haber cycle may also be represented as

$$\begin{tikzcd}
Na(s) \arrow[r, "\Delta U_{sub}"] & Na(g) \arrow[r, "\Delta U_{IE}"] & Na^+(g) \\
\tfrac{1}{2}Cl_2(g) \arrow[r, "\tfrac{1}{2}\Delta U_D"] \arrow[dr, "\Delta U_f"'] & Cl(g) \arrow[r, "\Delta U_{EA}"] & Cl^-(g) \arrow[dl, "\Delta U_{lattice}"] \\
& NaCl(s) &
\end{tikzcd}$$

Similar cycles can be constructed for enthalpy or any other thermodynamic property.

Example 17.1 Calculate the lattice energy of KCl from the following data:

(a) Enthalpy of sublimation of potassium = 90.9 kJ mol^{-1}
(b) Ionization energy of potassium = 418.7 kJ mol^{-1}
(c) Enthalpy of dissociation of chlorine = 240 kJ mol^{-1}
(d) Electron affinity of chlorine = −348.7 kJ mol^{-1}
(e) Enthalpy of formation of KBr = −440.3 kJ mol^{-1}

Solution The formation of KCl

$$K(s) + \tfrac{1}{2}Cl_2(g) \rightleftharpoons KCl(s) \qquad \Delta H_f = -440.3 \text{ kJ mol}^{-1}$$

may be represented by Born-Haber cycle as

$$\begin{tikzcd}
K\,(s) \arrow[d, "\Delta H_{\mathrm{sub}}"] & + \tfrac{1}{2}\,Cl_2\,(g) \arrow[d, "\tfrac{1}{2}\Delta H_{\mathrm{D}}"] \arrow[r, dashed, "\Delta H_f"] & KCl\,(s) \\
K\,(g) \arrow[d, "\Delta H_{\mathrm{IE}}"] & Cl\,(g) \arrow[d, "\Delta H_{\mathrm{EA}}"] & \\
K^+\,(g) & + \; Cl^-\,(g) \arrow[ruu, "\Delta H_{\mathrm{lattice}}"'] &
\end{tikzcd}$$

Now $\Delta H_f = \Delta H_{\mathrm{sub}} + \frac{1}{2}\Delta H_{\mathrm{D}} + \Delta H_{\mathrm{IE}} + \Delta H_{\mathrm{EA}} + \Delta H_{\mathrm{lattice}}$

$$-440.3 = 90.9 + \frac{240.0}{2} + 418.7 - 348.7 + \Delta H_{\mathrm{lattice}}$$

or $\Delta H_{\mathrm{lattice}} = -\,721.2 \text{ kJ mol}^{-1}$

EXAMPLE 17.2 The Born–Lande expression for lattice energy,

$$\Delta U_{\mathrm{lattice}} = -\frac{N_{\mathrm{A}}\, Z^2\, A\, e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

Calculate the lattice energy of NaCl from the following data:

Madelung constant $A = 1.748$,

Distance of separation $= 0.2814$ nm

Born exponent, $n = 8$,

$\varepsilon_0 = 8.854 \times 10^{-12}$,

$e = 1.602 \times 10^{-19}$ C

Solution **Lattice energy**

$$\Delta U_{\mathrm{lattice}} = -\frac{N_{\mathrm{A}}\, Z^2\, A\, e^2}{4\pi\varepsilon_0 r_0}\left(1 - \frac{1}{n}\right)$$

$N_{\mathrm{A}} = 6.022 \times 10^{23}$, $Z = 1$, $A = 1.748$, $e = 1.602 \times 10^{-19}$ C

$\varepsilon_0 = 8.854 \times 10^{-12}$, $n = 8$

$$\Delta U_{\mathrm{lattice}} = -\frac{6.022\times10^{23}\times(1)^2\times1.748\times(1.602\times10^{-19})^2}{4\times3.142\times8.854\times10^{-12}\times0.2814\times10^{-9}}\left(1-\frac{1}{8}\right)$$

$$= -\,862.7\times7/8$$

$$= -\,754.9 \text{ kJ mol}^{-1}$$

17.6 STRUCTURE OF IONIC COMPOUNDS—RADIUS RATIO RULE

The arrangement of ions in a crystal is greatly influenced by the ratio of the radii of the ions. The structures of many crystals can be determined by the relative numbers and sizes of the ions. For example, the limiting ratio for cations to fit in a trigonal site of anions is 0.225. The radius ratio r_c/r_a and permitted coordination numbers (the number of ions in contact with a particular ion) are given in Table 17.1.

TABLE 17.1 *Radius ratio (r_c/r_a) and structural arrangements*

Limiting r_c/r_a	*Coordination number*	*Structural arrangement*	*Example*
1–0.732	8	Cubic	CsCl
0.732–0.414	6	Octahedral	NaCl
0.414–0.225	4	Tetrahedral	ZnS
0.225–0.155	3	Triangular	Boron oxide

The structures of a few common compounds of the formula MX and MX_2 are described in terms of the close-packed arrangement of large anions with the small cations occupying interstitial sites, such as tetrahedral or octahedral (Table 17.2).

TABLE 17.2 *The structure of ionic solids*

Compound	*Coordination number*	*Description*	*Other Examples*
NaCl	$Na^+ = 6$ $Cl^- = 6$	ccp arrangement of Cl^-, Na^+ in all octahedral sites	Li, Na, K halides, AgCl, AgBr, MgO
ZnS (zinc blende)	$Zn^{2+} = 4$ $S^{2-} = 4$	ccp arrangement of S^{2-}, Zn^{2+} occupy alternate tetrahedral sites	BeS, CuCl, CuBr, CuI
ZnS (Wurtzite)	$Zn^{2+} = 4$ $S^{2-} = 4$	hcp arrangement of S^{2-}, Zn^{2+} occupy alternate tetrahedral sites	ZnO, CdS, BeO
CsCl	$Cs^+ = 8$ $Cl^- = 8$	simple cubic arrangement of Cl^-, Cs^+ in cubic sites	CsBr, CsI
CaF_2	$Ca^{2+} = 8$ $F^- = 4$	ccp arrangement of Ca^{2+}, F^- occupy all tetrahedral sites	SrF_2, BaF_2, CdF_2, MgF_2
CdI_2	$Cd^{2+} = 6$ $I^- = 3$	hcp arrangement of I^-, Cd^{2+} occupy octahedral sites between every second layer	

EXAMPLE 17.3 The radii of Rb^+, Br^- and I^- ions are 1.48 Å, 1.95 Å and 2.16 Å, respectively. With the help of the radius ratio rule, predict whether RbBr and RbI will adopt the structure of CsCl, NaCl, ZnS or boron oxide.

Solution The most probable structure can be predicted from the radius ratio rule

$$r(Rb^+) = 1.48\ \text{Å};\quad r(Br^-) = 1.95\ \text{Å}$$

$$\frac{r_c}{r_a} = \frac{r(Rb^+)}{r(Br^-)} = \frac{1.48}{1.95} = 0.759$$

Since the radius ratio lies between 1 and 0.732, RbBr will have a cubic arrangement like CsCl.

$$r(Rb^+) = 1.48\ \text{Å},\ r(I^-) = 2.16\ \text{Å}$$

$$\frac{r_c}{r_a} = \frac{r(Rb^+)}{r(I^-)} = \frac{1.48}{2.16} = 0.685$$

Since the radius ratio lies between 0.732 and 0.414, RbI will have an octahedral arrangement and its structure will be like NaCl.

17.7 COVALENT BOND

A covalent bond is formed by the mutual sharing of electrons between combining atoms of the same or different elements. According to the orbital concept, a covalent bond is formed between two atoms when a half-filled valence orbital of one atom overlaps with a half-filled valence orbital of the other.

Depending upon the type of overlapping, covalent bonds may be classified into two types.

Sigma (σ) Bond

This type of bond is formed by the axial overlap, along the internuclear axis, of atomic orbitals on adjacent atom. This may be *s–s* overlapping; *s-p* overlapping or *p-p* overlapping, as shown in Fig. 17.1.

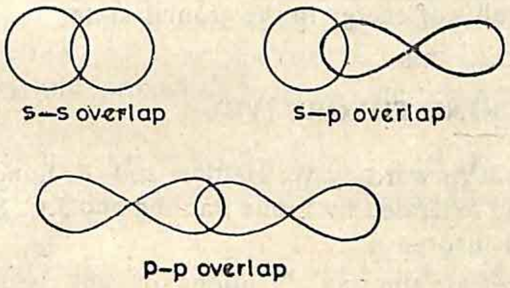


FIG. 17.1 *Formation of σ bonds by the axial overlap*

Pi (π) Bond

This type of bond is formed by the sidewise or the lateral overlap of half-filled atomic orbitals. This is shown in Fig. 17.2.

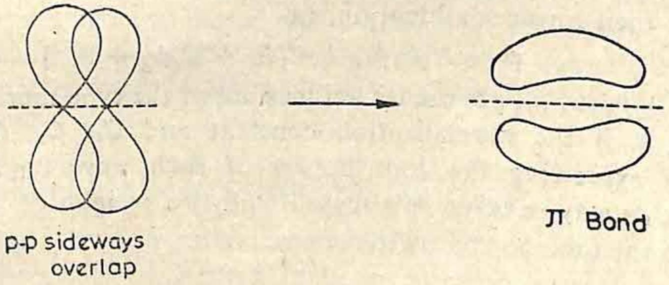


FIG. 17.2 *Formation of π bonds*

Due to the greater overlapping in their formation, σ bonds are stronger than π bonds.

17.8 WAVE MECHANICAL INTERPRETATION OF COVALENT BONDING

The theoretical treatment of bonding in molecules lies in the solution of the Schrödinger wave equation. However, it is very difficult to solve it for large molecules. To overcome the difficulties, certain approximations are made. The two main approaches are:

1. The Valence Bond Theory (VB)
2. The Molecular Orbital Theory (MO).

Both these approaches are based on the variation principle.

Variation Principle

The basic idea of the variation principle is that, if ψ_0 is the wave function for the ground state of the system, the energy corresponding to this wave function E_0 is always less than that associated with any other wave function that might be guessed. A better wave function gives an energy closer to value of energy in the ground state.

17.9 VALENCE BOND THEORY (VB)

This theory was put forward by W. Heitler and F. London (1927), and later improved and extended by Linus Pauling and J.C. Slater (1931). It is based upon two theorems:

1. If ψ_a and ψ_b are the wave functions for any two isolated independent atoms with energies E_a and E_b, respectively, then the total wave function ψ of the system is
$$\psi = \psi_a \times \psi_b \tag{17.3}$$
and energy, E of the system is
$$E = E_a + E_b \tag{17.4}$$
2. If a system can be represented by a number of wave functions $\psi_1, \psi_2, \psi_3, \ldots$, then it is best to represent the true wave function by their linear combination, i.e.
$$\psi = N[C_1\psi_1, + C_2\psi_2 + C_3\psi_3 + \ldots]$$

where $\psi_1, \psi_2, \psi_3, \ldots$, are the wave functions of the type represented by Eq. (17.3), N is the normalization constant and $C_1, C_2, C_3, \ldots$ are coefficients expressing the contribution of each wave function. The square of C_1's may be taken as a measure of the weight of each wave function in the total wave function.

17.10 APPLICATION OF VB THEORY TO H_2 MOLECULE

Consider a hydrogen molecule formed by two hydrogen atoms H_a and H_b having electrons (1) and (2), respectively. When the two atoms are brought close together to form a molecule, there will be interactions between them. The system may be expressed as:

$$^1H_a \quad ^2H_b$$

and wave function ψ_I (as first approximation) will be

$$\psi_I = \psi_a(1)\,\psi_b(2)$$

where ψ_a and ψ_b represent the wave functions of two hydrogen atoms H_a and H_b, respectively.

The bond energy of the above system, calculated as a function of the internuclear distance, is only 25.1 kJ mol^{-1} (the total energy of the two isolated atoms is assumed to be zero). This value is much lower than the experimental bond energy for the formation of H_2 molecule, which is 431.7 kJ mol^{-1}.

First Improvement—Exchange Energy

When a molecule is formed, atomic orbitals overlap and it is not correct to label electrons as they became indistinguishable. Consequently, a state in which electron (1) is near nucleus H_b and electron (2) is near nucleus H_a is equally probable. Hence, the system may also be represented as:

$^2H_a\ ^1H_b$ and $\psi_{II} = \psi_a(2)\,\psi_b(1)$ State II

Now, if the system may be represented by wave functions ψ_I and ψ_{II}, the true wave function ψ is

$$\psi = C_1\psi_I + C_2\psi_2 = C_1[\psi_a(1)\,\psi_b(2)] + C_2[\psi_a(2)\,\psi_b(1)]$$

Since states I and II are equally probable, their contributions must be equal, i.e.

$$C_1^2 = C_2^2 \quad \text{or} \quad C_1 = \pm C_2$$

and if $C_1 = 1$, $C_2 = \pm 1$ (for simplicity)

$$\therefore\ \psi_+ = \psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1) \quad (C_1 = 1, C_2 = 1)$$

$$\psi_- = \psi_a(1)\,\psi_b(2) - \psi_a(2)\,\psi_b(1) \quad (C_1 = 1, C_2 = -1)$$

ψ_+ is a symmetric combination and represents the bonding state. Its bonding energy is 320.8 kJ mol^{-1}. The additional lowering of energy (equal to $320.8 - 25.1 = 277.7$ kJ mol^{-1}) is called *exchange energy*. ψ_- is called dissymmetric combination and represents the *repulsive state*. ψ_+ is also called *covalent wave function*.

Second Improvement—Use of Effective Nuclear Charge

The wave function was improved by considering the screening effect of electrons. The improved wave function gave a bonding energy of 338 kJ mol^{-1}.

Third Improvement—Ionic Character

The wave function was improved by considering the ionic character, in which both electrons may be with either H_a or H_b.

III state $H_a^{1,2}$ H_b $\psi_{III} = \psi_a(1)\,\psi_a(2)$

IV state H_b $H_b^{1,2}$ $\psi_{IV} = \psi_b(1)\,\psi_b(2)$

so that $\psi_{\text{ionic}} = \psi_a(1)\,\psi_a(2) + \psi_b(1)\,\psi_b(2)$

By taking both ionic and covalent wave functions together,

$$\psi = C_3\,\psi_{\text{covalent}} + C_4\,\psi_{\text{ionic}}$$

or $$\psi = C_3[\psi_a(1)\,\psi_b(2)+\psi_a(2)\,\psi_b(1)]+C_4[\psi_a(1)\,\psi_a(2)+\psi_b(1)\,\psi_b(2)]$$

where C_3 and C_4 give contributions of covalent and ionic terms. For the H_2 molecule, C_3/C_4 has been found to be 6/1 and bonding energy is 361.8 kJ mol^{-1}.

Other Improvements

Many other corrections were applied to the wave function to get bonding energy close to the experimental value. For example:

James and Coolidge (used 13 terms):	Bond energy = 430 kJ mol^{-1}
Kolos and Roothan (used 50 terms):	Bond energy = 431.7 kJ mol^{-1}

17.11 CONCEPT OF RESONANCE

The concept of resonance is introduced as a result of the development of the VB treatment of bonding in molecules. The concept of resonance may be summarised as:

When a molecule cannot be represented by a single structure, and its various characteristics can be described by two or more different structures, the true structure is said to be a *resonance hybrid* of these structures.

The individual structures are called *resonating structures* or *canonical structures*. The resonance hybrid is more stable than any one of the contributing structures. The extra stability of the resonance hybrid, as compared to the most stable (having lowest energy) of the contributing structures, is called *resonance energy*.

Rules for Writing Resonating Structures

1. The contributing structures should have the same relative positions of atoms. They should differ only in the position of electrons.
2. The contributing structures should have the same number of unpaired electrons.
3. The contributing structures should not differ much in energy.
4. Contributing structures in which negative charge resides on electronegative atom and positive charge resides on electropositive atoms are closer to the true structure.
5. Contributing structures should be so written that unlike charges reside on adjacent atoms.

6. Contributing structures with the greater number of covalent bonds contribute more to the real structure.

Some Common Examples

O_2 molecule

$$:\ddot{O}::\ddot{O}: \longleftrightarrow :\overset{+}{\ddot{O}}:\underset{..}{\overset{-}{\ddot{O}}}: \longleftrightarrow :\underset{..}{\overset{-}{\ddot{O}}}:\overset{+}{\ddot{O}}:$$

Best represented by $:O \overset{\cdots}{\underset{\cdots}{—}} O:$

(One single covalent bond and two three-electron bonds. Each three-electron bond has the strength of one half of a normal covalent bond.)

N_2 molecule

$$:N:::N: \longleftrightarrow \overset{-}{:}\ddot{N}::\overset{+}{N}: \longleftrightarrow \overset{+}{:}N::\overset{-}{\ddot{N}}:$$

CO molecule

$$:C::\ddot{O}: \longleftrightarrow \overset{-}{:}C:::\overset{+}{O}: \longleftrightarrow :\overset{+}{C}:\underset{..}{\overset{-}{\ddot{O}}}:$$

CO_2 molecule

$$:\ddot{O}::C::\ddot{O}: \longleftrightarrow :\underset{..}{\overset{-}{\ddot{O}}}:C:::\overset{+}{O}: \longleftrightarrow \overset{+}{:}O:::C:\underset{..}{\overset{-}{\ddot{O}}}:$$

17.12 MOLECULAR ORBITAL THEORY

According to this theory, developed by Hunds and Mulliken, electrons in molecules are considered to move in orbitals associated with several nuclei. These orbitals are called *molecular orbitals.* To construct M.O.'s, the simplest approach is known as the *linear combination of atomic orbitals* (LCAO) approach.

According to this approach, whenever two atomic orbitals are brought closer, they combine to form a molecular orbital. The wave function of the molecular orbital may be written as a suitable combination of atomic orbitals (ψ_A and ψ_B) as:

$$\psi^{MO} = a\psi_A + b\psi_B$$

a and b are the weightage coefficients. For two identical atoms (homonuclear molecules),

$$a^2 = b^2 \quad \text{or} \quad a = \pm b$$

Thus, we can have two molecular orbitals as

$$\psi = \psi_A + \psi_B \quad \text{(bonding M.O.)}$$
$$\psi = \psi_A - \psi_B \quad \text{(antibonding M.O.)}$$

Every electron in a bonding M.O. contributes to attraction. The bonding M.O. possesses lower energy than the atomic orbital from which it is formed. On the other hand, an antibonding M.O. contributes to the repulsion between two atoms and has higher energy than the atomic orbitals from which it is formed. For example, the 1s atomic orbitals of two atoms combine to form two molecular orbitals labelled as $\sigma_1 s$ (bonding) and $\sigma_1 s^*$ (antibonding). Similarly, 2s atomic orbitals combine to form σ_{2s} and σ_{2s}^* M.O.'s. Of the 2p orbitals, $2p_z$ orbitals form sigma orbitals (z-axis assumed the molecular axis) $\sigma 2p_z$ and $\sigma 2p_z^*$, whereas $2p_x$ and $2p_y$ orbitals form π orbitals; $\pi 2p_x$, $\pi 2p_y$, $\pi 2p_x^*$ and $\pi 2p_y^*$.

Energy-Level Diagram for Molecular Orbitals

There are two types of energy-level diagrams:

(i) For molecules up to N_2 (where the difference in energies of 2s and 2p orbitals is small) :

$$\sigma_{1s},\ \sigma_{1s}^*,\ \sigma_{2s},\ \sigma_{2s}^*,\ \pi 2p_x = \pi 2p_y,\ \sigma 2p_z,\ \pi 2p_x^* = \pi 2p_y^*,\ \sigma 2p_z^*$$

(ii) For molecules after N_2,

$$\sigma_{1s},\ \sigma_{1s}^*,\ \sigma_{2s},\ \sigma_{2s}^*,\ \sigma 2p_z,\ \pi 2p_x = \pi 2p_y,\ \pi 2p_x^* = \pi 2p_y^*,\ \sigma 2p_z^*$$

Information Obtained from M.O. Diagrams

(a) *Bond order* It may be expressed as

½ [No. of electrons in bonding M.O.'s − No. of electrons in antibonding M.O.'s

Bond order helps to predict bond length and bond strength. With increase in bond order, bond length decreases while bond strength increases.

(b) *Magnetic properties* The molecular orbital diagram can also predict whether the molecule is diamagnetic (all paired electrons) or paramagnetic (unpaired electrons).

Molecular orbital configurations, magnetic character and bond order of some common molecules are summarized in Table 17.3.

17.13 ELECTRONEGATIVITY AND POLARITY IN COVALENT BONDS

Electronegativity may be defined as the tendency of an atom to attract the shared pair of electrons within a molecule towards itself. In a bond between two atoms with different electronegativities, the more electronegative atom attracts the shared electrons more strongly. As a result, the centres of positive and negative charges of the system do not coincide. One end of the bond acquires a partial negative charge (δ-) and

TABLE 17.3 *Molecular orbital configuration*, bond order and magnetic character of some molecules*

Species	*Molecular orbital configuration*	*Bond order*	*Magnetic character*
H_2	$(\sigma_{1s})^2$	1	Diamagnetic
H_2^+	$(\sigma_{1s})^1$	$\frac{1}{2}$	Paramagnetic
He_2^+	$(\sigma_{1s})^2\ (\sigma^*_{1s})^1$	$\frac{1}{2}$	Paramagnetic
He_2	$(\sigma_{1s})^2\ (\sigma^*_{1s})^2$	Does not exist	—
Li_2	$KK\ (\sigma_{2s})^2$	1	Diamagnetic
Be_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2$	Does not exist	—
B_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^1\ (\pi 2p_y)^1$	1	Paramagnetic
C_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2$	2	Diamagnetic
N_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$	3	Diamagnetic
N_2^+	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$	$2\frac{1}{2}$	Paramagnetic
O_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\overset{*}{\pi} 2p_x)^1\ (\overset{*}{\pi} 2p_y)^1$	2	Paramagnetic
O_2^+	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\overset{*}{\pi} 2p_x)^1$	$2\frac{1}{2}$	Paramagnetic
O_2^-	$KK\ (\sigma_{2s})^2\ (\sigma^+_{2s})^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\overset{*}{\pi} 2p_x)^2\ (\overset{*}{\pi} 2p_y)^1$	$1\frac{1}{2}$	Paramagnetic
F_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\overset{*}{\pi} 2p_x)^2\ (\overset{*}{\pi} 2p_y)^2$	1	Diamagnetic
Ne_2	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\sigma 2p_z)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\pi \overset{*}{2} p_x)^2\ (\pi \overset{*}{2} p_y)^2\ (\sigma 2\overset{*}{p}_z)^2$	Does not exist	—
CN	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^1$	$2\frac{1}{2}$	Paramagnetic
CN^-	$KK\ (\sigma_{2s})^2\ (\sigma^*_{2s})^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_x)^2$	3	Diamagnetic
NO	$KK\ (\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2\ (\pi \overset{*}{2} p_x)^1$	$2\frac{1}{2}$	Paramagnetic
NO^+	$KK\ (\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$	3	Diamagnetic
CO	$KK\ (\sigma_{2s})^2\ (\sigma_{2s}^*)^2\ (\pi 2p_x)^2\ (\pi 2p_y)^2\ (\sigma 2p_z)^2$	3	Diamagnetic

**KK* represents molecular orbitals of 1s orbitals, i.e., $KK = (\sigma 1s)^2\ (\sigma \overset{*}{1} s)^2$

the other end gets a partial positive charge (δ^+). Such a bond is called a polar covalent bond. For example,

$$\underset{\text{Non-polar}}{H : H} \qquad \overset{\delta+}{H}\text{——}\overset{\delta-}{Cl} \qquad \overset{\delta+}{I}\text{ —— }\overset{\delta-}{Cl}$$

Polar molecules

The extent of polar character of a bond is determined by the electronegativity difference of the bonding atoms.

Dipole Moment

For a diatomic molecule, the product of the magnitude of charge on each atom and the distance between them is called the dipole moment. This can be determined experimentally. Its value provides a measure of the polar character of a molecule. The dipole is a vector quantity and is represented by an arrow (+→) pointing from the positive centre towards the negative centre.

The dipole moment gives valuable information about the structures of molecules. In case of polyatomic molecules, the dipole moment is the vector sum of the dipole moments of various bonds. The magnitude of the resulting dipole moment is dependent upon the spatial orientation of various bonds present in the molecule. If a molecule is symmetrical, the resultant dipole moment of the molecule is zero. The dipole moments of some common molecules are shown in Fig. 17.3.

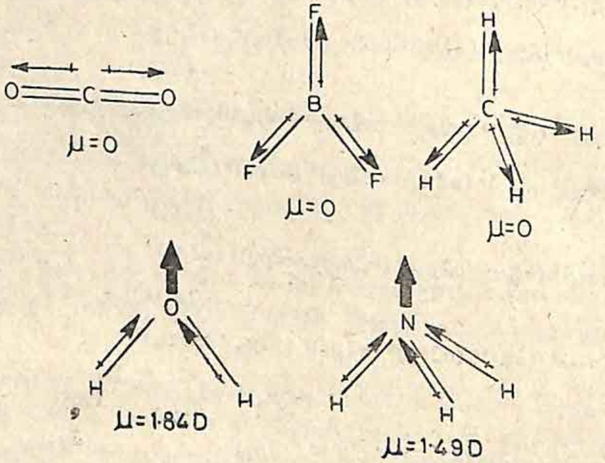
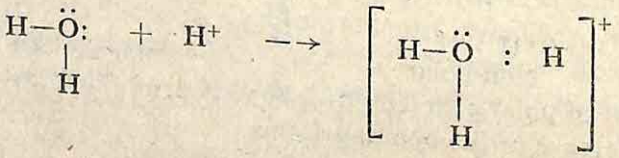


FIG. 17.3 *Dipole moment of some polyatomic molecules*

17.14 COORDINATE OR DATIVE BOND

This is a special case of covalent bond. It is formed by the mutual sharing of electrons between two atoms, with the shared pair of electrons being contributed by one atom while the other merely participates in sharing. For example, in the formation of the hydronium ion (H_3O^+), a coordinate bond is formed between the oxygen atom of the water molecule and a proton:



$$\begin{array}{c}\text{H}-\ddot{\text{O}}:\\ \phantom{\text{H}-}|\\ \phantom{\text{H}-}\text{H}\end{array} + \text{H}^+ \longrightarrow \left[\begin{array}{c}\text{H}-\ddot{\text{O}} : \text{H}\\ |\\ \text{H}\end{array}\right]^+$$

It is important to note that, in hydronium ions, all three O—H bonds are equivalent.

17.15 METALLIC BOND

Metals are characterised by bright lustre, high electrical and thermal conductivity, malleability, ductility and high tensile strength. A simple model to explain the nature of bonding in metals is the electron sea model.

Electron Sea Model

In this model, a metal is assumed to consist of positive kernels arranged on a regular lattice, surrounded by mobile electrons which move freely within the boundaries of the crystal. Alternatively, it is supposed that there is a sea of valence electrons in which kernels are immersed. The simultaneous forces of attraction between the mobile electrons and positive kernels is responsible for holding the metal atoms together and is known as *metallic bonds*.

An alternative approach for the metallic bond is the *band model*. This is based upon the molecular orbital theory. According to this two atomic orbitals combine to form two molecular orbitals. Similarly, *N* atoms with one atomic orbital on each atom combine to give *N* molecular orbitals with energies so close that they may be treated as an energy band. The formation of an energy band depends upon:

1. the close proximity of a large number of atoms
2. the energy difference between pure atomic orbitals

The idea of energy bands gives a pictorial representation of the energy levels in a metallic crystal. The arrangement of electrons in the different

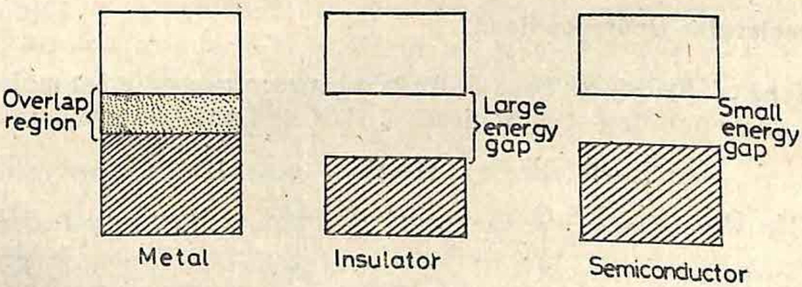


FIG. 17.4 *Energy gap in a metal, a semiconductor and an insulator*

energy bands determines the characteristics of a metal. The energy bands formed from different atomic orbitals may overlap or be separated from each other. The spaces between bands represent energies forbidden to electrons in metals and are called *energy gaps*. The energy gaps of metals, insulators and semiconductors are shown in Fig. 17.4. In metals, the higher energy empty states necessary for electrical conduction are close to filled bands, so electrons can go into the empty bands. On the other hand, the energy gap between the filled and unfilled bands is very large in the case of insulators. Therefore the empty bands are not accessible, for conduction, to the electrons in the filled bands. Several solids have properties between metals and non-metals. These are called *semiconductors*. The energy gap in these substances is very small and the increase in temperature gives enough thermal energy for some of the electrons in the filled bands to move into the empty ones. For example, the energy gap in silicon is only 104.6 kJ mol^{-1} and it behaves as semiconductor while the energy gap in carbon, which is an insulator, is 502 kJ mol^{-1}.

17.16 HYDROGEN BOND

When hydrogen is bonded to a highly electronegative atom (such as F, O or N), it can form an additional bond to another electronegative atom. This additional bond is called a hydrogen bond. Thus, a hydrogen bond is formed when a hydrogen atom serves as a bridge between two highly electronegative atoms, holding one by a covalent bond and the other by a hydrogen bond. For example, in HF,

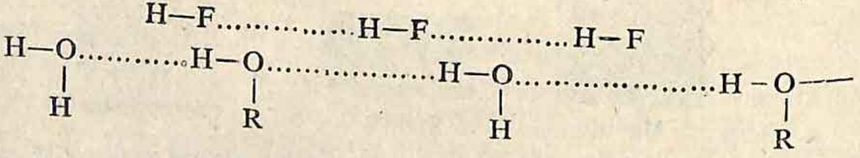
$$\cdots\cdots H{-}F\cdots\cdots H{-}F\cdots\cdots H{-}F\cdots\cdots$$

The hydrogen bond is a very weak bond with a strength of about 8 to 42 kJ mol^{-1}. Due to the presence of hydrogen bonds, compounds containing hydrogen attached to electronegative atoms (e.g. HF, H_2O, NH_3) exhibit unexpected properties such as relatively high melting and boiling points.

Hydrogen bonds can be classified into two categories.

Intermolecular Hydrogen Bond

This type of hydrogen bond is formed between two different molecules of the same or different substances.



$$H{-}F\cdots\cdots H{-}F\cdots\cdots H{-}F$$

$$\underset{\displaystyle H}{H{-}\underset{|}{O}}\cdots\cdots\underset{\displaystyle R}{H{-}\underset{|}{O}}\cdots\cdots\underset{\displaystyle H}{H{-}\underset{|}{O}}\cdots\cdots\underset{\displaystyle R}{H{-}\underset{|}{O}}{-}{-}$$

Intramolecular Hydrogen Bond

This type of bond is formed between a hydrogen atom and an electronegative atom within the same molecule. For example as shown in Fig. 17.5, o-nitrophenol and o-fluorophenol show intramolecular hydrogen bonding. The effect of intramolecular hydrogen bonding on physical properties is opposite to that of intermolecular hydrogen bonding.

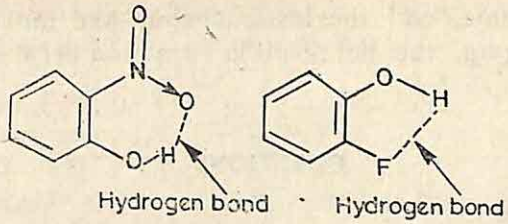


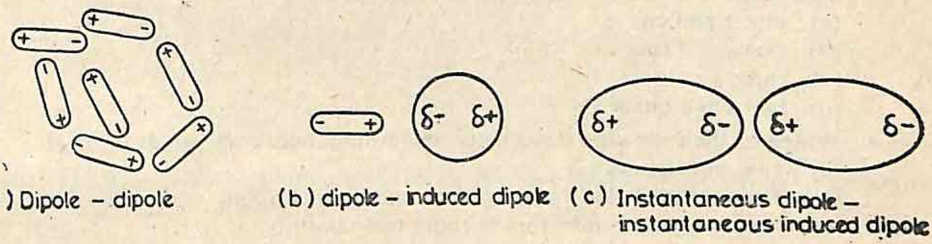
FIG. 17.5 *Intramolecular hydrogen bonds in o-nitrophenol and o-fluorophenol.*

17.17 VAN DER WAALS FORCES

Van der Waals forces are the weakest but most universal. There are three main types of forces which contribute to van der Walls bonding.

Attractive Forces among Polar Molecules which Arise due to Dipole–Dipole Interactions

These are the result of electrostatic attraction between oppositely charged ends of molecules (Fig. 17.6a).



(a) Dipole – dipole (b) dipole – induced dipole (c) Instantaneous dipole – instantaneous induced dipole

FIG. 17.6 *Interactions between molecules*

Attractive Forces between a Molecule with a Permanent Dipole and a Molecule (or Atom) without a Dipole

Due to the presence of a polar molecule, the electron cloud in the neighbouring non-polar molecule gets distorted towards the positive end of the dipole molecule. This leads to an induced dipole in the nonpolar molecule, resulting in an attractive interaction between the permanent and induced dipoles (Fig. 17.6b).

Attractive Forces between Non-polar Molecules or Atoms

These forces arise as a result of motion of electrons in non-polar molecules or monoatomic gases (e.g. He, Ne). To understand the origin of these forces, let us consider two helium atoms, very close together. Due to the motion of the electrons, the electron distribution in an atom is unsymmetrical at any given instant, with a slight increase in electron density on one side. As a result, one end of the atom acquires agslight negative charge while the other end acquires a slight positive charge, leading to an instantaneous dipole. This momentary dipole influences the electron distribution in the neighbouring atom and induces an instantaneous induced dipole. Although this effect (Fig. 17.6c) persists for a very short time, and the instantaneous and induced dipoles are constantly changing, the net result is attraction between neighbouring atoms.

QUESTIONS

QUIZ QUESTIONS

Type A: Multiple Choice

17.1 An ionic compound A^+B^- is most likely to be formed when
- (a) the ionization energy of A is high and electron affinity of B is low
- (b) the ionization energy of A is low and electron affinity of B is high
- (c) both, the ionization energy of A and electron affinity of B are high
- (d) both, the ionization energy of A and electron affinity of B are low

17.2 Which of the following statements concerning a covalent bond is false?
- (a) The electrons are shared between atoms
- (b) The bond is non-directional
- (c) The strength of the bond depends upon the extent of overlapping
- (d) The bond formed may be polar or non-polar

17.3 The number of bonds in a nitrogen molecule is
- (a) one σ and one π
- (b) one σ and two π
- (c) three σ only
- (d) two σ and one π

17.4 Which of the following statements concerning ionic compounds is false?
- (a) They consist of ions
- (b) They generally have high melting and boiling points
- (c) They are good conductors at room temperature
- (d) They are generally soluble in polar solvents

17.5 The weakest bond among the following is
- (a) ionic
- (b) covalent
- (c) metallic
- (d) hydrogen bond

17.6 Which of the following conditions is not correct for resonating structures?
- (a) The contributing structures must have the same number of unpaired electrons
- (b) The contributing structures should have similar energies
- (c) The contributing structures should be so written that unlike charges reside on atoms that are far apart
- (d) The positive charge should be present on the electropositive element and the negative charge on the electronegative element

17.7 The hydrogen molecule may be represented by two wave functions. ψ_{covalent} and ψ_{ionic} and C_1 and C_2 are coefficient indicating the weight of each function. The real wave function may be written as (N is the normalization constant)
- (a) $\psi = N[\psi_{\text{covalent}} + \psi_{\text{ionic}}]$
- (b) $\psi = N[C_1\,\psi_{\text{covalent}} + C_2\,\psi_{\text{ionic}}]$
- (c) $\psi = N[C_1\,\psi_{\text{covalent}} \times C_2\,\psi_{\text{ionic}}]$
- (d) $\psi = (C_1 + C_2)\,N[\psi_{\text{covalent}} + C_2\,\psi_{\text{ionic}}]$

17.8 If ψ_a and ψ_b are the wave functions of two hydrogen atoms with electrons 1 and 2, respectively, the wave function may be written as $\psi_1 = \psi_a(1)\,\psi_b(2)$, When the improved function becomes $\psi_2 = \psi_a(1)\,\psi_b(2) + \psi_a(2)\,\psi_b(1)$ a significant lowering in energy occurs, known as

(a) resonance energy
(b) ionic energy
(c) exchange energy
(d) shielding energy

17.9 A molecule may be represented by three structures having energies E_1, E_2 and E_3, respectively. The energies of these structures follow the order $E_3 < E_2 < E_1$, respectively. If the experimental bond energy of the molecule is E_0, the resonance energy is

(a) $(E_1 + E_2 + E_3) - E_0$
(b) $E_0 - E_3$
(c) $E_0 - E_1$
(d) $E_2 - E_0$

17.10 Which of the following resonating structures is not correct for CO_2?

(a) $:\underset{..}{O} = C = \overset{..}{O}:$

(b) $:\underset{..}{\overset{..}{O}}{}^{-} - C \equiv \overset{+}{O}:$

(c) $:\underset{..}{\overset{+}{O}} - C \equiv \underset{..}{O}\overset{-}{:}$

(d) $:\overset{+}{O} \equiv C - \underset{..}{\overset{..}{O}}\overset{-}{:}$

17.11 The carbon monoxide molecule may be represented by the following structures except

(a) $:C::\overset{..}{O}:$

(b) $\overset{-}{:}C:::O\overset{+}{:}$

(c) $:\overset{+}{C}:\underset{..}{\overset{..}{O}}\overset{-}{:}$

(d) ${}^{+}C:::\underset{..}{O}\overset{-}{:}$

17.12 Which of the following combinations are not allowed in the LCAO method for the formation of a MO (consider the z axis as the molecular axis)

(a) $s + p_z$
(b) $s + p_y$
(c) $p_x + p_x$
(d) $p_z + p_z$

17.13 The bond order in O_2^+ is the same as in

(a) N_2^+
(b) CN^-
(c) NO^+
(d) CO

17.14 The molecular orbital configuration of B_2 molecule is

(a) $KK\,(\sigma\,2s)^2\,(\overset{*}{\sigma}\,2s)^2\,(\pi\,2p_x)^1\,(\pi\,2p_y)^1$

(b) $KK\,(\sigma\,2s)^2\,(\overset{*}{\sigma}\,2s)^2\,(\sigma\,2p_z)^2$

(c) $KK(\sigma\,2s)^2(\sigma\,\overset{*}{2s})^2(\pi\,2p_x)^2$

(d) $KK(\sigma\,2s)^2(\overset{*}{\sigma}\,2s)^2(\sigma\,2p_z)^1(\pi\,2p_x)^1$

17.15 In which set of molecules are all the species paramagnetic?
(a) B_2, O_2, N_2
(b) B_2, O_2, NO
(c) B_2, F_2, O_2
(d) B_2, O_2, Li_2

17.16 The calculated bond order in the superoxide (O_2^-) ion is
(a) 2.5 (b) 2
(c) 1.5 (d) 1

17.17 Which has the smallest bond length?
(a) O_2 (b) $^+_2$
(c) O_2^- (d) O_2^{2-}

17.18 If the z-axis is the molecular axis, then π molecular orbitals are formed by the overlap of
(a) $s + p_z$ (b) $p_x + p_y$
(c) $p_z + p_z$ (d) $p_x + p_x$

17.19 In which set of diatomic molecules is the bond order of each member $2\frac{1}{2}$?
(a) N_2^+, NO, O_2^+
(b) O_2^+, NO, CN^-
(c) N_2^+, CN, O_2^+
(d) CN^-, N_2^+, N_2

17.20 The bond energies in NO, NO^+ and NO^- follow the order
(a) $NO^+ > NO > NO^-$
(b) $NO > NO^+ > NO^-$
(c) $NO^- > NO > NO^+$
(d) $NO^+ > NO^- > NO$

17.21 The bond order in the species O_2, O_2^- and O_2^+ is correctly represented by
(a) $O_2 > O_2^- > O_2^+$
(b) $O_2^+ > O_2^- > O_2$
(c) $O_2^+ > O_2 > O_2^-$
(d) $O_2^- > O_2 > O_2^+$

17.22 Which of the following species is diamagnetic?
(a) O_2^+ (b) NO^+
(c) NO (d) O_2

17.23 Which of the following molecules has unpaired electrons in antibonding molecular orbitals?

(a) O_2 (b) N_2
(c) C_2 (d) B_2

17.24 Which of the following statements is not correct regarding bonding molecular orbitals ?
(a) Bonding molecular orbitals possess less energy than the atomic orbitals from which they are formed.
(b) Bonding molecular orbitals have low electron densities between the two nuclei.
(c) Every electron in bonding molecular orbitals contributes to the attraction between atoms.
(d) They are formed when the lobes of the combining atomic orbitals have the same sign.

17.25 The sequence of energy levels of M.O.'s formed from the outermost shells of C_2 molecule is

(a) $\sigma 2s < \sigma 2\overset{*}{s} < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi 2\overset{*}{p}_x = \pi \overset{*}{2} p_y < \sigma \overset{*}{2} p_z$

(b) $\sigma 2s < \sigma 2\overset{*}{s} < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \sigma 2\overset{*}{p}_z < \pi \overset{*}{2} p_y = \overset{*}{\pi} 2p_x$

(c) $\sigma 2s < \sigma 2\overset{*}{s} < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi 2\overset{*}{p}_x = \pi \overset{*}{2} p_y < \sigma \overset{*}{2} p_z$

(d) $\sigma 2s < \sigma 2\overset{*}{s} < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \sigma 2\overset{*}{p}_z < \pi 2\overset{*}{p}_x = \pi \overset{*}{2} p_y$

17.26 The molecular orbital configuration of CN^+ is

(a) $KK\,(\sigma 2s)^2\,(\sigma 2\overset{*}{s})^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$

(b) $KK\,(\sigma 2s)^2\,(\sigma 2\overset{*}{s})^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^1\,(\pi 2p_y)^1$

(c) $KK\,(\sigma 2s)^2\,(\sigma 2\overset{*}{s})^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^1$

(d) $KK\,(\sigma 2s)^2\,(\sigma 2\overset{*}{s})^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$

17.27 According to radius ratio rule a compound consisting of cations of radius 0.97 Å and anions of radius 2.51 Å will probably crystalize in the form
(a) CsCl (b) NaCl
(c) ZnS (d) CaF_2

17.28 In the formation of NO^+ from NO, the electron is removed from
(a) a σ orbital (b) a π orbital
(c) a σ^* orbital (d) a π^* orbital

17.29 The maximum radius ratio r_A/r_B for an atom A to fit into the simple cubic B lattice is
(a) 1 (b) 0.732
(c) 0.414 (d) 0.155

17.30 CaO and NaCl have the same crystal structure and approximately the same ionic radii. If U is the lattice energy of NaCl, the approximate lattice energy of CaO is
(a) $U/2$ (b) U
(c) $2U$ (d) $4U$

17.31 The magnitude of the lattice energy of a solid increases if
(a) the ions are large
(b) the ions are small
(c) the ions are of equal size
(d) charges on the ions are small

17.32 Which of the following molecules has zero dipole moment ?
(a) NH_3 (pyramidal)
(b) $CHCl_3$ (tetrahedral)
(c) H_2O (angular)
(d) BF_3 (triangular)

17.33 The electronegativities of F, Cl, Br and I are 4, 3, 2.8 and 2.5, respectively. Which of the hydrogen halides has a high percentage of ionic character ?
(a) HF
(b) HCl
(b) HBr
(d) HI

17.34 Which of the following molecules has a high dipole moment ?
(a) CO_2 (linear)
(b) CCl_4 (tetrahedral)
(c) H_2S (angular)
(d) BF_3 (triangular)

17.35 In which of the following pairs does the first compound not have a higher boiling point than the second ?
(a) Kr, Ne
(b) HBr, HCl
(c) NH_3, PH_3
(d) Cl_2, KCl

17.36 Which of the following compounds has the least tendency to form hydrogen bonds between molecules ?
(a) NH_3
(b) NH_2OH
(c) HF
(d) CH_3F

17.37 In which of the following set of molecules is the order of boiling points incorrect ?
(a) Xe > Ar > He
(b) HF > HCl > HBr
(c) $H_2O > H_2Se > H_2S$
(d) $C_3H_8 > C_2H_6 > CH_4$

17.38 Intermolecular forces in solid hydrogen are
(a) electrostatic forces
(b) hydrogen bonds
(c) van der Waals forces
(d) metallic bonds

17.39 The boiling point of water (H_2O) is 100°C whereas that of hydrogen sulphide (H_2S) is −42°C. This can be attributed to
(a) a larger bond angle in H_2O than H_2S
(b) smaller size of oxygen atom as compared to sulphur
(c) larger ionization energy of oxygen than sulphur
(d) larger tendency of H_2O to form hydrogen bonds than H_2S

17.40 Which of the following statements is correct ?
(a) A σ bond is weaker than a π bond
(b) There are four coordinate bonds in the NH_4^+ ion
(c) The covalent bond is directional in nature
(d) HF is less polar than HCl

Type B: True or False

17.41 A σ bond is stronger than a π bond.

17.42 The three-electron bond in the oxygen molecule (proposed by Pauling) is assumed to be equivalent to one and a half of a normal two-electron bond.

17.43 A σ_p molecular orbital always has lower energy than the related π_p molecular orbital.

17.44 The bond order in the species O_2, O_2^+ and O_2^- decreases as

$$O_2^+ > O_2 > O_2^-$$

17.45 The bond energy in a diatomic molecule always increases when an electron is lost.

17.46 Electrons in antibonding M.O. contribute to repulsion between two atoms.

17.47 Out of NO, NO^+ and NO^-, only NO is paramagnetic.

17.48 The bond order in CO and CN^- is the same.

17.49 The nature of the bond between hydrogen and chlorine in the HCl molecule in the vapour phase is ionic.

17.50 With increase in bond order, bond length decreases and bond strength increases.

Type C: Fill in the Blanks

17.51 Each molecular orbital, whether bonding or antibonding, can accommodate a maximum of ———— electrons.

17.52 Sidewise overlap of two *p*-orbitals leads to the formation of ———— molecular orbital.

17.53 Molecular orbitals with cylindrical symmetry are called ———— molecular orbitals.

17.54 The bond order in the H_2^+ molecule ion is ————.

17.55 In the CO molecule there are ———— valence electrons and the configuration is the same as that of ———— molecule.

17.56 The bond order in B_2 molecule is ———— and in Be_2 molecule is ————.

17.57 In the process $O_2^+ \longrightarrow O_2^{2+} + e$, the electron is lost from ———— molecular orbital.

17.58 Every electron in a ———— M.O. contributes to the attraction between two atoms.

17.59 Sigma bond is formed by ———— overlap of atomic orbitals.

17.60 The bond order in the N_2^+ ion is ———— than that of the N_2 molecule, whereas that of O_2^+ ion is ———— than that of the O_2 molecule.

ANSWERS

17.1 (b) *17.2* (b) *17.3* (b) *17.4* (c) *17.5* (d) *17.6* (c) *17.7* (b)
17.8 (c) *17.9* (b) *17.10* (c) *17.11* (d) *17.12* (b) *17.13* (a) *17.14* (a)
17.15 (b) *17.16* (c) *17.17* (b) *17.18* (d) *17.19* (c) *17.20* (a) *17.21* (c)
17.22 (b) *17.23* (a) *17.24* (b) *17.25* (a) *17.26* (a) *17.27* (c) *17.28* (d)
17.29 (b) *17.30* (d) *17.31* (b) *17.32* (d) *17.33* (a) *17.34* (c) *17.35* (d)
17.36 (d) *17.37* (b) *17.38* (c) *17.39* (d) *17.40* (c) *17.41* True *17.42* True
17.43 False *17.44* True *17.45* False *17.46* True *17.47* True *17.48* True
17.49 False *17.50* True *17.51* Two *17.52* π *17.53* σ *17.54* $\frac{1}{2}$ *17.55* 10, NO^+
17.56 one, zero; does not exist *17.57* antibonding π orbital *17.58* bonding
17.59 axial *17.60* less, more

18

Molecular Structure and Spectroscopy

The determination of molecular structure has been the central problem in chemistry. Though many techniques have been developed for structure determination, spectroscopic methods have dominated in the recent years. The study of molecular spectra has provided very valuable information regarding the structure of molecules.

18.1 ENERGY LEVELS IN MOLECULES

The total energy of a molecule, besides its translational energy, may be considered to be the sum of electronic (ε_e), vibrational (ε_v) and rotational (ε_r) energies:

$$\varepsilon = \varepsilon_e + \varepsilon_v + \varepsilon_r \qquad (18.1)$$

Equation (18.1) implies that there is no interaction between the various degrees of freedom. These energies are quantized and each one of them has discrete values. The relative energies of various levels are shown in Fig. 18.1. The electronic energy levels are represented by n. Within the electronic energy level there are vibrational energy levels represented by ν (e.g. $\nu = 0, 1, 2, \ldots$). The vibrational energy levels consist of a number of rotational energy levels designated by J(e.g. $J = 0, 1, 2, \ldots$).

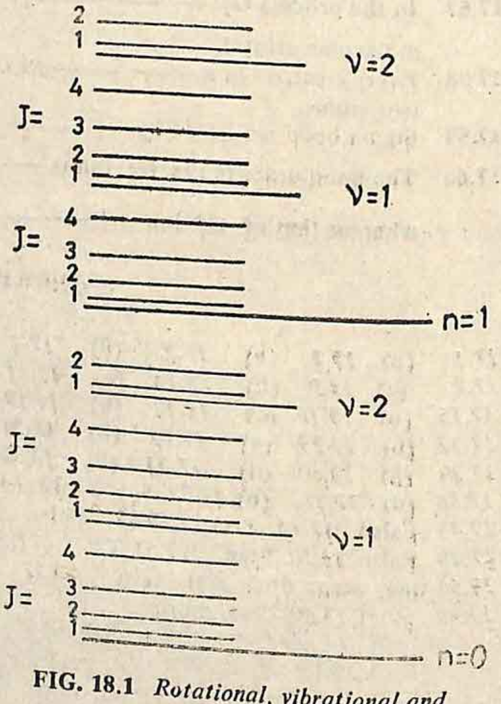


FIG. 18.1 *Rotational, vibrational and electronic energy levels*

18.2 TYPES OF MOLECULAR SPECTRA

Depending upon the transitions in electronic, vibrational and rotational energy levels, three types of molecular spectra are obtained.

Rotational Spectrum

The rotational spectrum is obtained by transitions in rotational energy levels. The energy changes involved in this type of spectrum are small and, therefore, these transitions occur in the *far infrared region* or *microwave region.*

Vibrational–Rotational Spectrum

The transitions in vibrational energy levels are also accompanied by changes in rotational energy levels. As a result, the spectrum obtained is called a *vibrational–rotational spectrum.* This is obtained in the *infrared region.*

Electronic Band Spectrum

The transitions between electronic energy levels are also accompanied by vibrational and rotational transitions. Thus, the spectrum obtained is complex and looks like a continuous band due to overlapping of rotational, vibrational and electronic transitions. This is observed in the *visible* and *ultraviolet regions.*

18.3 ROTATIONAL SPECTRA

These spectra are obtained for molecules with permanent dipole moments. Let us consider diatomic molecules. These may be regarded as rigid rotators. The energy E_r of such a rigid rotator, in any given rotational energy level J, is given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \qquad J = 0, 1, 2, \ldots \tag{18.2}$$

where I is the moment of inertia of the molecule defined as

$$I = \mu r_0^2$$

where μ is the reduced mass of the molecule and r_0 is the internuclear distance. If m_1 and m_2 are the atomic masses of the two atoms A and B, then

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

so that

$$I = \left(\frac{m_1 m_2}{m_1 + m_2}\right) r_0^2 \tag{18.3}$$

When a transition occurs from the rotational energy level J to a higher rotational level J', the energy difference between these levels will be given by

$$\Delta E = E_{J'} - E_J = \frac{h^2}{8\pi^2 I}\left[J'(J'+1) - J(J+1)\right] \quad (18.4)$$

According to the selection rules for pure rotational spectra of diatomic molecules, the transitions are only observed between the levels $\Delta J = \pm 1$. Thus if $\Delta J = J' - J = 1$, then

$$\Delta E = \frac{h^2}{8\pi^2 I}(2J)$$

Now $$\Delta E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

or $$\bar{\nu} = \left(\frac{h}{8\pi^2 Ic}\right)2J \quad (18.5)$$

For a given molecule, $h/8\pi^2 Ic$ is constant and is called the *rotational constant*, denoted by B. Thus,

Wave number, $\bar{\nu} = 2BJ$ (18.6)

Thus, for $\bar{\nu}_1 \rightarrow 0 = 2B$

$\bar{\nu}_2 \rightarrow 1 = 4B$

$\nu_3 \rightarrow 2 = 6B$

This means that the spectral lines in rotational spectra are equally spaced, with spacing equal to $2B$. This is also known as *frequency separation*.

Rotational spectra can be used to calculate the moments of inertia and bond lengths of diatomic molecules.

Polyatomic Molecules

The spectra of linear triatomic molecules show the same characteristic separation of $2B$. For example, linear triatomic molecules like COS, behave like the HCl molecules. However, it has been observed that the B values are quite small and consequently, the lines are more closely spaced. The spectra of these molecules are studied in the microwave region to calculate B and the moment of inertia. As the number of bonds in a linear triatomic molecule is two, the bond distances cannot be determined from a single B value. In such cases, B values are obtained for isotopically substituted molecules (such as $O^{16}-C^{12}-S^{32}$ and $O^{16}-C^{12}-S^{34}$) and both the bond distances can be determined.

Expression for Non-Rigid Rotation

We have assumed that diatomic molecules behave as rigid rotators. However, this assumption is not always valid because all bonds are elastic to some extent. To account for this, the expression for rotational energy was improved as

$$E_r = BJ(J+1) - DJ^2(J+1)^2 \qquad (18.7)$$

where D is called the *centrifugal distortion constant.* It takes into account the increase in bond length due to the rotation of the molecule.

Example 18.1 The rotational spectrum of HI shows a series of equidistant lines separated by 12.8 cm^{-1}. Calculate the moment of inertia and the internuclear bond length (atomic mass of H = 1 and I = 127).

Solution

In a rotational spectrum, the frequency separation is $2B$.

$$2B = 12.8 \text{ cm}^{-1} \text{ or } B = 6.4 \text{ cm}^{-1}$$

But $\quad B = \dfrac{h}{8\pi^2 Ic}$

or Moment of inertia, $I = \dfrac{h}{8\pi^2 Bc}$

$$h = 6.626 \times 10^{-27} \text{ erg s},\ B = 6.4 \text{ cm}^{-1},\ c = 3 \times 10^{10} \text{ cm s}^{-1}$$

$$I = \frac{6.626 \times 10^{-27} \text{ erg s}}{8 \times \left(\frac{22}{7}\right)^2 \times (6.4 \text{ cm}^{-1}) \times (3 \times 10^{10} \text{ cm s}^{-1})}$$

[erg = g cm^2 s^{-2}]

$$= 4.37 \times 10^{-40} \text{ g cm}^2$$

Now, $\quad I = \mu \cdot r_0^2$

Mass of an atom of H $= \dfrac{1}{6.022 \times 10^{23}}$ g

Mass of an atom of I $= \dfrac{127}{6.022 \times 10^{23}}$ g

$$\text{or} \quad \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\frac{1}{6.022 \times 10^{23}} \times \frac{127}{6.022 \times 10^{23}}}{\frac{1}{6\ 022 \times 10^{23}}(1 + 27)}$$

$$= 1.65 \times 10^{-24} \text{ g}$$

$$\therefore \quad r_0^2 = \frac{I}{\mu} = \frac{4.37 \times 10^{-40} \text{ g cm}^2}{1.65 \times 10^{-24} \text{ g}} = 2.648 \times 10^{-16} \text{ cm}^2$$

$$\therefore \quad r_0 = 1.627 \times 10^{-8} \text{ cm}$$

Example 18.2 (SI Units) The rotational spectrum of the NO molecule showed a frequency difference between successive lines equal to 332 m^{-1}. Calculate the internuclear bond length (atomic mass of $N = 14 \times 10^{-3}$ kg mol^{-1}, O = 16×10^{-3} kg mol^{-1}, $h = 6.626 \times 10^{-34}$ J s, $C = 3 \times 10^8$ m s^{-1}).

Solution

Frequency separation $= 2B$

$$2B = 332 \text{ m}^{-1} \text{ or } B = 166 \text{ m}^{-1}$$

Now, $B = \dfrac{h}{8\pi^2 Ic}$

or $I = \dfrac{h}{8\pi^2 Bc}$

$$I = \frac{6.626 \times 10^{-34}\ \text{J s}}{8 \times \left(\frac{22}{7}\right)^2 \times (166\ \text{m}^{-1}) \times (3 \times 10^8\ \text{m s}^{-1})}$$

$$= 1.68 \times 10^{-46}\ \text{kg m}^2$$

But $I = \left(\dfrac{m_1 m_2}{m_1 + m_2}\right) r_0^2$

$$m_1 = \frac{14 \times 10^{-3}}{6.022 \times 10^{23}}\ \text{kg}, \qquad m_2 = \frac{16 \times 10^{-3}}{6.022 \times 10^{23}}\ \text{kg}$$

$$1.68 \times 10^{-46}\ \text{kg m}^2 = \frac{14 \times 10^{-3} \times 16 \times 10^{-3}\ \text{kg}}{6.022 \times 10^{23}\,(16 + 14) \times 10^{-3}}\ r_0^2$$

$$1.68 \times 10^{-46}\ \text{kg m}^2 = 1.24 \times 10^{-26}\ \text{kg}\ r_0^2$$

$$r_0^2 = \frac{1.68 \times 10^{-46}}{1.24 \times 10^{-26}} = 1.355 \times 10^{-20}\ \text{m}^2$$

$$= 1.164 \times 10^{-10}\ \text{m} = 0.1164\ \text{nm}$$

EXAMPLE 18.3 The bond length of HF molecule is 0.918 Å. Calculate the frequencies in cm^{-1} for the lines in the rotational spectrum of HF for the transitions $J = 0 \rightarrow J = 1$; $J = 1 \rightarrow J = 2$; $J = 2 \rightarrow J = 3$.

Solution Frequency separation $= 2\,B$

$$B = \frac{h}{8\pi^2\, Ic}$$

where $I = \left(\dfrac{m_1 m_2}{m_1 + m_2}\right) r_0^2$

$$r_0 = 0.918\ \text{Å} = 0.198 \times 10^{-8}\ \text{cm}, \quad m_1 = \frac{1}{6.022 \times 10^{23}}\ \text{g}$$

$$m_2 = \frac{19}{6.022 \times 10^{23}}\ \text{g}$$

$$I = \frac{1 \times 19}{6\ 02 \times 10^{23}\,(1 + 19)} \times (0.918 \times 10^{-8})^2$$

$$= 1.329 \times 10^{-40}\ \text{g cm}^2$$

$$B = \frac{h}{8\pi^2\, Ic}$$

$$= \frac{6.626 \times 10^{-27}\ \text{erg s}}{8\,(22/7) \times (1.329 \times 10^{-40}\ \text{g cm}^2) \times (3 \times 10^{10}\ \text{cm s}^{-1})}$$

$$= 21\ \text{cm}^{-1}$$

Wave numbers for different transitions:

$J = 0 \longrightarrow J = 1$, $2\,B = 2 \times 21 = 42\ \text{cm}^{-1}$
$J = 1 \longrightarrow J = 2$, $2\,B \times 2 = 84\ \text{cm}^{-1}$
$J = 2 \longrightarrow J = 3$, $2\,B \times 3 = 126\ \text{cm}^{-1}$

18.4 VIBRATION-ROTATION SPECTRA

These spectra are exhibited by molecules in which there is change in dipole moment. The vibrations of a diatomic molecule may be assumed to be simple harmonic. The vibrational energy is given by

$$E_v = (v + \tfrac{1}{2})\, h\nu_0 \tag{18.8}$$

where v is the vibrational quantum number and may take values ($v = 0, 1, 2, \ldots$), h is Planck's constant, ν_0 is the fundamental vibrational frequency. When the oscillating molecule is in its lowest vibrational level, $v = 0$, its energy

$$E_0 = \tfrac{1}{2}\, h\nu_0 \tag{18.9}$$

is known as the *zero point energy*. This is present even at absolute zero.

When a transition occurs from vibrational energy level v to a higher vibrational level v', the energy difference is given as

$$\Delta E_v = E_v' - E_v = (v'+\tfrac{1}{2})\, h\nu_0 - (v+\tfrac{1}{2})\, h\nu_0 = (v'-v)\, h\nu_0 \tag{18.10}$$

But vibrational transitions are also accompanied by rotational transitions, so rotational changes may also be added or subtracted:

$$\Delta E = \Delta E_v \pm \Delta E_r$$

$$\Delta E = h\nu = (v'-v)\, h\nu_0 \pm \left(\frac{h^2}{4\pi^2 I}\right) J \tag{18.11}$$

The frequency,

$$\nu = (v'-v)\, \nu_0 \pm \left(\frac{h}{4\pi^2 I}\right) J$$

or

$$\nu = \Delta v\, \nu_0 \pm \left(\frac{h}{4\pi^2 I}\right) J \tag{18.12}$$

Generally $\Delta v = 1$

This means that the vibrational-rotational spectrum of a molecule will not consist of a single line corresponding to the vibrational transition Δv, but will have a number of lines on either side of the expected position due to the addition and subtraction of the rotational contribution. From the above equation, it is cleart hat when rotational energy

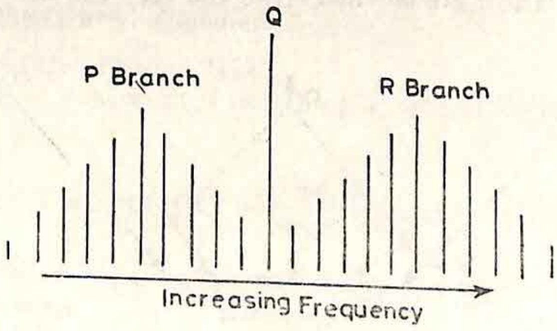


FIG. 18.2 *Vibrational-rotational spectrum of a diatomic molecule*

contributions are added, we get a series of lines on the high-frequency side (called *R* branch), and when the rotational contributions are subtracted, we get a series of lines on the low-frequency side (called *P* branch). This is shown in Fig. 18.2.

Force Constant

If the vibrations of a diatomic molecule are assumed to be simple harmonic, the restoring force per unit displacement (called force constant) can be calculated from the relation:

$$k = 4\pi^2 \nu_0^2 C^2 \frac{m_1 m_2}{m_1 + m_2} \tag{18.13}$$

Knowing the values of various constants, the force constant (K) can be calculated.

Anharmonicity

Real molecules do not obey the conditions of harmonic oscillation. To account for the anharmonicity. Equation (18.8) may be modified as

$$E_v = (v+\tfrac{1}{2})\, h\nu_0 - (v+\tfrac{1}{2})^2\, xh\nu_0 \tag{18.14}$$

where x is the anharmonicity constant. Due to anharmonicity the spacing between vibrational energy levels decreases with increase in the vibrational quantum number. By measuring the progressive decrease, the value of x can be calculated.

Vibrational Spectra of Polyatomic Molecules

Polyatomic molecules exhibit a complicated vibrational motion. This motion can be described in terms of a number of *normal modes* or *normal vibrations*. In polyatomic molecules containing N atoms, there are $3N$-6 normal modes of vibration in non-linear molecules and $3N$-5 in linear molecules. These normal modes can be described in terms of normal coordinates (i.e. bond lengths or bond angles). For example, the normal vibrational modes for the linear CO_2 molecule and angular H_2O are:

H_2O molecule An angular water molecule, H_2O should have $3 \times 3 - 6 = 3$ normal modes. These are labelled ν_1, ν_2 and ν_3. The first two are

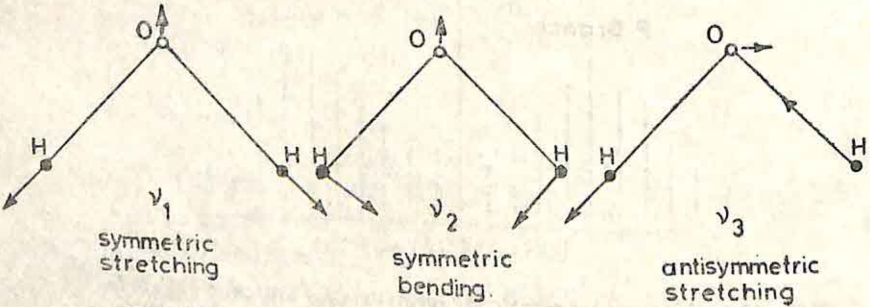


FIG. 18.3 *Normal modes of vibration for H_2O molecule*

symmetric and the third is antisymmetric.

CO_2 molecules Linear triatomic molecule have four normal modes of vibration. These are:

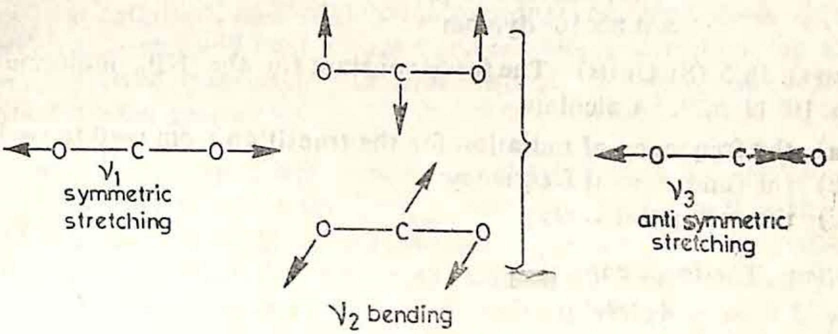


FIG. 18.4 *Normal modes of vibration for CO_2 molecule*

In this case, ν_2 has two vibrations which have identical value of ν and are called doubly degenerate.

The vibrational spectrum is observed if the transition occurs in any vibrational mode or any combination of vibrational modes involved. When the transition occurs in any one of the vibrational quantum numbers from $\nu = 0$ to $\nu = 1$, all others remaining zero or unchanged, these are called *fundamental bands*, i.e. from ν (0, 0, 0, . . .) to ν=(1, 0, 0, . . .) or (0,1,0, . . .) or (0, 0, 1, . . .). Since the vibrations are not truly harmonic, the selection rule $\Delta\nu = 1$ is not always obeyed. As a result, many weak bands arise from transitions in which $\Delta\nu = +2$, $+3$, , . . . If the transition is from $\nu = 0$ to $\nu = 2$, the band obtained is called the *first overtone*, i.e. ν (0, 0, 0, . . .) $\longrightarrow$ ν (2, 0, 0). However, if more than one vibrational quantum number changes, the band obtained is called a combination band, i.e. ν (0, 0, 0, . . .) $\longrightarrow$ ν (0, 1, 1) or ν (0, 1, 2, . . .) or ν (1, 2, 3).

Example 18.4 The fundamental vibrational frequency of the HCl molecule is 2886 cm^{-1}. Calculate

(a) the reduced mass of HCl

(b) the force constant for stretching in HCl, in dynes cm^{-1}.

Solution

(a) Reduced mass of HCl $= \dfrac{m_H\, m_{Cl}}{m_H + m_{Cl}}$

$$m_H = \frac{1}{6.022 \times 10^{23}},\quad m_{Cl} = \frac{35.5}{6.022 \times 10^{23}}$$

$$\text{Reduced mass} = \frac{1 \times 35.5}{6.022 \times 10^{23}\,(1 + 35.5)} = 1.62 \times 10^{-24}\ \text{g}$$

(b) Now, $k = 4\pi^2\nu^2c^2\ \mu$

$$= 4\times\left(\frac{22}{7}\right)^2\times(2886\ \text{cm}^{-1})^2\times(3\times10^{10}\ \text{cm s}^{-1})^2$$
$$\times(1.62\times10^{-24}\ \text{g})$$
$$= 4.8\times10^5\ \text{dyn cm}^{-1}$$

EXAMPLE 18.5 (SI Units) The force constant for the HBr molecule is 4.13×10^2 N m^{-1}. Calculate

(a) the frequency of radiation for the transition from $v=0$ to $v=1$
(b) the fundamental frequency
(c) the zero point energy

Solution The force const[illegible]

$$k = 4\pi^2c^2\nu^2\ \mu$$

or
$$\nu = \frac{1}{2\pi\, c}\sqrt{\frac{k}{\mu}}$$

$$c = 3\times10^8\ \text{m s}^{-1},\quad k = 4.13\times10^2\ \text{N m}^{-1}$$

$$\mu = \frac{m_\text{H}\ m_\text{Br}}{m_\text{H}+m_\text{Br}} = \frac{1\times80}{6.022\times10^{23}\ (1+80)} = 1.64\times10^{-27}\ \text{kg}$$

(i) $$\nu = \frac{1}{2\times(22/7)\times(3\times10^8)}\times\left(\frac{4.13\times10^2}{1.64\times10^{-27}}\right)^{\frac{1}{2}}$$
$$= 2.66\times10^5\ \text{m}^{-1}$$

(ii) Fundamental frequency $\nu_0 = \nu\times c$

$$= (2.66\times10^5\ \text{m}^{-1})\times(3\times10\ \text{m s}^{-1})$$
$$= 7.98\times10^{13}\ \text{s}^{-1}$$

(iii) Zero point energy $= \frac{1}{2}\,h\,\nu_0$

$$= \tfrac{1}{2}\times(6.626\times10^{-34}\ \text{J s}^{-1})\times(7.98\times10^{13}\ \text{s}^{-1})$$
$$= 5.29\times10^{-20}\ \text{J}$$

18.5 ELECTRONIC SPECTRA

Electronic spectra arise when an electron in a molecule jumps from one energy level to another. During transition in electronic energy levels, changes in vibrational and rotational energy levels may also take place. As a result, each band in the electronic spectrum consists of a number of fine lines due to vibrational and rotational transitions and thus appears continuous. If E and E' are the energies of the molecule in the initial and the final states,

$$E = E_e+E_v+E_r$$
$$E' = E'_e+E'_v+E'_r$$

The change of energy, ΔE, for the electronic transition is

$$\Delta E = (E'_e-E_e)+(E'_v-E_v)+(E'_r-E_r)$$
$$= \Delta E_e+\Delta E_v+\Delta E_r$$

The frequency of radiation is

$$\nu = \frac{\Delta E_e + \Delta E_v + \Delta E_r}{h}$$

Now, ΔE_v and ΔE_r may have a number of different values depending upon the rotational and vibrational quantum numbers involved. The resulting spectra will have a large number of lines corresponding to the given electron transition. In other words, the spectrum will be a complex band spectrum.

In case of polyatomic molecules, electrons are present in sigma bonding (σ) and antibonding (σ^*), pi bonding (π) and antibonding (π^*), and non-bonding molecular (n) orbitals (Chemical Bonding, Ch. 17). Electronic transitions occur when the electrons are excited from bonding or non-bonding molecular orbitals to antibonding molecular orbitals as

$$\sigma \longrightarrow \sigma^*,\ n \longrightarrow \pi^*,\ n \longrightarrow \sigma^*,\ \pi \longrightarrow \pi^*$$

18.6 RAMAN SPECTRA, RAMAN EFFECT

Raman found that when a monochromatic light of definite frequency (ν) is passed through a gas, liquid or solid, and the scattered light is observed at right angles to the incident beam, the scattered radiation may also contain lines of frequency lower or higher than the original frequency. This is known as Raman effect. The lines of lower frequency are called *Stokes lines* and those of higher frequency are called *anti-Stoke's lines*. Raman also observed that the difference ($\Delta\nu$) between the incident frequency (ν) and any scattered frequency (ν') is constant and characteristic of the substance exposed to light. This difference is called the *Raman frequency* and is independent of the frequency of the incident light.

The Raman effect can be used to find vibrational and rotational transitions in homonuclear and heteronuclear molecules. This effect is not exhibited only by polar molecules, but also by non-polar molecules such as H_2, N_2, Cl_2, etc. In a vibrational spectrum, the modes which change the polarizability are Raman active. In rotational Raman scattering, the selection rule for rotational lines is $\Delta J = \pm 2$. Therefore, the energy difference between two levels is

$$\Delta E_r = Bh\,[J'\,(J'+1) - J''\,(J''+1)]$$

but $\quad J' - J'' = 2$

so that

$$\Delta E_r = Bh\,[4J' - 2]$$

This means that spectral lines will be equally spaced with a frequency separation equal to $4B$.

QUESTIONS

Numerical Problems

18.1 The rotational spectra of HBr and HCl give a series of lines with an equidistant separation of 16.9 cm^{-1} and 20.7 cm^{-1}, respectively. Calculate

(a) their moments of inertia

(b) the internuclear distances of the molecules

18.2 (SI Units) The spectrum of BrF gives $B = 0.357\ cm^{-1}$. Calculate the bond length of the molecule.

18.3 (SI Units) The rotational spectrum of HF shows a series of equidistant lines spaced 4190 m^{-1} apart. Calculate the moment of inertia and bond length of the HF molecule.

18.4 The bond length of the CO molecule is 1.13 Å. Calculate the frequencies, in cm^{-1}, required for transitions in rotational quantum numbers $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ and $3 \rightarrow 4$.

18.5 The series of lines in the rotational spectrum of HI are equally separated by 12.8 cm^{-1}. Calculate the frequencies corresponding to transitions in the rotational quantum numbers $0 \rightarrow 1$, $1 \rightarrow 2$, $2 \rightarrow 3$ and $3 \rightarrow 4$.

18.6 The fundamental vibrational frequency ($\nu_0 \rightarrow 1$) bond for CO is 2140 cm^{-1}. Calculate the force constant for the molecule.

18.7 (SI Units) The force constant for hydrogen fluoride is $9.7 \times 10^2\ N\ m^{-1}$. Calculate its fundamental frequency and zero point energy.

18.8 How many normal vibrational modes are possible for

(a) HF

(b) CO_2 (linear)

(c) SO_2 (bent)

(d) NH_3

18.9 A mercury line of 4360Å is used to study the Raman spectrum of the HCl molecule. Calculate the wavelength of Stokes-Raman line if the fundamental vibrational frequency of HCl, $\nu_0 \rightarrow 1 = 2886\ cm^{-1}$.

18.10 Which of the following vibrations are i.r. active?

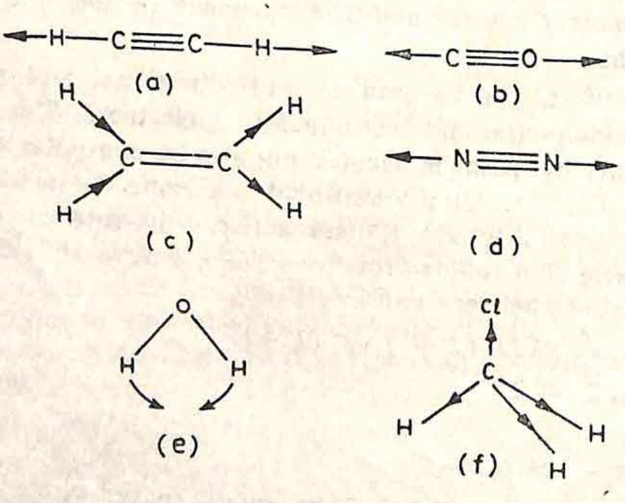


FIG. 18.5

QUIZ QUESTIONS

Type A: Multiple Choice

18.11 Rotational spectra are observed in the

(a) near infrared region
(b) far infrared region
(c) visible region
(d) ultraviolet region

18.12 In the rotational spectra of diatomic molecules, the spacing between successive lines is equal to (I is moment of inertia)

(a) $\dfrac{h}{4\pi^2 Ic}$ (b) $2\left(\dfrac{h}{4\pi^2 Ic}\right)$

(c) $\dfrac{h}{4\pi^2 Ic^2}$ (d) $\dfrac{4h}{\pi^2 Ic}$

18.13 If ν is the vibrational quantum number and ν_0 is the fundamental frequency (in cm^{-1}), the vibration energy is given by

(a) $E_v = \frac{1}{2} hc\, \nu_0$
(b) $E_v = (v - \frac{1}{2})h\, \nu_0$
(c) $E_v = (v + \frac{1}{2})h\, \nu_0$
(d) $E_v = (v + \frac{1}{2})hc\, \nu_0$

18.14 The zero point energy of a molecule is (ν_0 = fundamental frequency in cm^{-1})

(a) $h\, \nu_0$
(b) $\frac{1}{2}\, h\, \nu_0$
(c) $\frac{1}{2}\, hc\, \nu_0$
(d) $(\nu + \frac{1}{2})\, hc\, \nu_0$

18.15 The selection rule for transitions in rotational energy levels of a diatomic molecule is

(a) $\Delta J = +1$
(b) $\Delta J = -1$
(c) $\Delta J = \pm 1$
(d) $\Delta J = \pm 2$

18.16 If ν is the fundamental frequency, μ the reduced mass and k the force constant, then

(a) $k = \dfrac{1}{2\pi}\sqrt{\dfrac{\mu}{\nu}}$

(b) $\nu = \dfrac{1}{2\pi}\sqrt{\dfrac{k}{\mu}}$

(c) $\nu = 4\pi^2 k^2 \mu$

(d) $\nu = \dfrac{k}{\mu}\sqrt{\dfrac{1}{2\pi}}$

18.17 The difference between the incident and scattered frequencies in the Raman spectrum is called the

(a) Stoke's line
(b) anti-Stoke's line
(c) Raman frequency
(d) *P*-branch

18.18 Which of the following relationship is correct regarding molecular energy levels.

(a) E(electronic) > E(vibrational) > E(rotational)
(b) E(rotational) > E(vibrational) > E(electronic)

(c) E(electronic) > E(rotational) > E(vibrational)
(d) E(vibrational) > E(electronic) > E(rotational)

18.19 Which of the following diatomic molecules will not give a rotational spectrum?

(a) NO (b) HF
(c) N_2 (d) CO

18.20 The selection rule for the transition in rotational energy levels in the Raman spectrum is

(a) $\Delta J = \pm 1$
(b) $\Delta J = +1$
(c) $\Delta J = +2$
(d) $\Delta J = \pm 2$

Type B: Multiple Choice (Numerical Problems)

18.21 The vibrational spectrum of HCl give

Transition	$\nu_0 \rightarrow \nu_1$	$\nu_1 \rightarrow \nu_2$	$\nu_2 \rightarrow \nu_3$	$\nu_3 \rightarrow \nu_4$
$\bar{\nu}$ (cm^{-1})	2880	5668	8347	10923

The fundamental frequency is

(a) 2788 cm^{-1}
(b) 8.64×10^{13} s^{-1}
(c) 1.04×10^{12} s^{-1}
(d) 28.80 m^{-1}

18.22 The fundamental vibration frequency of H_2 is approximately

(a) half that of D_2
(b) 1.414 times that of D_2
(c) twice that of D_2
(d) half that of D_2

18.23 In the rotational spectrum of NO, the series of lines are equally spaced by 3.326 cm^{-1}. The frequency corresponding to the transition $J_{2\rightarrow 3}$ is

(a) 3.326 cm^{-1} (b) 6.652 cm^{-1}
(c) 9.978 cm^{-1} (d) 1.109 cm^{-1}

18.24 If the rotational spectrum of HF has lines 41.9 cm^{-1} apart. The moment of inertia of HF is

(a) $\dfrac{6.626 \times 10^{-27}}{41.9 \times (22/7)^2 \times (3 \times 10^{10})}$

(b) $\dfrac{6.626 \times 10^{-27}}{8 \times (41.9)^2 \times (22/7)^2 \times (3 \times 10^{10})}$

(c) $\dfrac{6.626 \times 10^{-27}}{4 \times (41.9) \times (22/7)^2 \times (3 \times 10^{10})}$

(d) $\dfrac{(6.626 \times 10^{-27})^2}{4 \times (41.9) \times (22/7)^2 \times (3 \times 10^{10})}$

18.25 If HCl is irradiated with radiation of frequency 68.8×10^{13} s^{-1}, and the fundamental vibrational frequency of HCl is 86.0×10^{12} s^{-1}, then the Stokes–Raman line will be observed at

(a) 60.2×10^{13} s^{-1}
(b) 77.4×10^{13} s^{-1}
(c) $68.8 \times 10^{13} - (3 \times 10^{10}) \times (86 \times 10^{12})$
(d) $\dfrac{(68.8 - 8.6) \times 10^{13}}{6.626 \times 10^{-27}}$

Type C: True or False

18.26 In the Raman spectrum the Stokes lines have higher frequencies than the anti-Stoke's lines.

18.27 Electronic band spectra are observed in visible and ultraviolet regions.

18.28 The spectral lines in rotational spectra are equally spaced with spacing equal to $h/8\pi^2Ic$.

18.29 When a transition occurs from vibrational energy level v to a higher vibration level v', the energy difference is given by $(v' - v)\, h\nu_0$.

18.30 In a polyatomic linear molecule with N atoms, there are $3N$-6 normal modes of vibration.

18.31 For the vibrational quantum number change $\nu(0, 0, 0) \rightarrow \nu(2, 0, 0)$, the band obtained is called an overtone.

18.32 In rotational Raman scattering, the selection rule for rotational lines is $\Delta J = \pm 1$.

18.33 Vibrational transitions are always accompanied by electronic transitions.

18.34 Raman frequency is independent of the frequency of incident light and is characteristic only of the substance exposed to the incident light.

18.35 The force constant for a diatomic molecule is inversely proportional to the vibrational frequency.

Type D: Fill in the Blanks

18.36 The vibrational rotational spectrum is observed in ———— region.

18.37 When the oscillating molecule is in its lowest vibrational level, its energy is equal to ———— and is called ———— .

18.38 In the Raman spectrum, the lines scattering at right angles with frequencies lower than the original are called ————, while those with higher frequencies are called ———— .

18.39 The vibrational transitions in polyatomic molecules,
$\nu(0, 0, 0) \longrightarrow \nu(0, 0, 2)$ and $\nu(0, 0, 0) \longrightarrow \nu(0, 1, 2)$
are called ———— and ————, respectively.

18.40 In a rotational spectrum, transitions are only observed between rotational energy levels of $\Delta J =$ ———— .

ANSWERS

Numerical Problems

18.1 (a) 3.308×10^{-40} (b) 1.42 Å *18.2* 0.176 nm *18.3* 0.0918 nm *18.4* 3.84, 7.68, 11.52, 15.36 *18.5* 12.8, 25.6, 38.4, 51.2 *18.6* 1.85×10^6 dyn cm^{-1} *18.7* 1.25×10^{14}, 4.13×10^{-20} J *18.8* (i) 1 (ii) 4 (iii) 3 (iv) 6 *18.9* 49.9×10^{-7} cm^{-1} *18.10* (b), (c), (e), (f).

Quiz Questions

18.11 (b) *18.12* (a) *18.13* (d) *18.14* (c) *18.15* (c) *18.16* (b) *18.17* (c) *18.18* (a) *18.19* (c) *18.20* (d) *18.21* (b) *18.22* (b) *18.23* (c) *18.24* (c) *18.25* (a) *18.26* False *18.27* False *18.28* True *18.29* True *18.30* False *18.31* True *18.32* False: selection rule for Raman spectrum is $\Delta J = \pm 2$ *18.33* False: accompanied by rotational transitions *18.34* True *18.35* False *18.36* near infrared *18.37* $\frac{1}{2} hc\, \nu_0$, zero point energy *18.38* Stoke's, anti-Stoke's lines *18.39* overtone, combination band *18 40* ± 1

19

Statistical Thermodynamics

The laws of thermodynamics and their applications were discussed in Chapters 4 to 8. These laws do not make any reference to the structure of matter and are applicable only to macroscopic systems. Classical thermodynamics neither offers any justification for the existence of these laws nor a method for direct calculations of thermodynamic properties. Any thermodynamic property is either to be measured directly or calculated from measured quantities using appropriate relations.

Statistical mechanics deals with the calculations of macroscopic properties (energy, entropy, etc.) of a system from microscopic properties (mass of molecules, their energy levels and intermolecular potential). It also justifies the laws of thermodynamics. It is a vast subject, but here we are restricted to the statistical thermodynamics of ideal gases.

19.1 MACROSCOPIC AND MICROSCOPIC STATES OF A SYSTEM

By a system we mean a thermodynamic system assumed to consist of a large number of particles (atoms, molecules, ions, electrons, etc.). In the thermodynamic or macroscopic sense, the system is characterized by a few thermodynamic variables like V, T, p, etc. While the microscopic state of a system is defined by the wave function ψ obtained by solution of the Schrödinger equation, in practice it is never possible to obtain such a ψ as it is a function of the coordinates of all nuclei and electrons of all molecules in the system. However, in principle, we can assume the existence of such microscopic states. Corresponding to a macroscopic state, there is a very large number of microscopic states. The observed macroscopic property is the average of its value in all accessible states in the system. If X_i is the property in the ith microscopic state, and P_i is the probability of finding the system in that microscopic state, the average value X which will be observed experimentally is given by

$$<X> = \sum_i P_i X_i \tag{19.1}$$

19.2 PROBABILITY OF A MICROSCOPIC STATE

If we consider a thermodynamically isolated system at equilibrium, then the number of molecules N, volume V, and energy E (within the uncertainty limit) remain constant. Corresponding to this energy level, the system can exist in a large number of quantum (microscopic) states Ω. All these states are equally probable and hence the probability of each state is $1/\Omega$ and

$$<X> = \Sigma\, P_i X_i = \Sigma \frac{1}{\Omega} X_i = \frac{1}{\Omega} \Sigma\, X_i \tag{19.2}$$

It has been shown that the entropy of the system is given by

$$S = k_b \ln \Omega \tag{19.3}$$

i.e. the larger the number of microscopic states corresponding to a macroscopic state, the larger will be its entropy. In practice, we don't deal with isolated systems. Generally, we deal with systems at constant temperature and constant volume or constant pressure. The probability P_i of finding a system (with N molecules and volume V, in equilibrium with the thermal source at temperature T) in the energy state E_i is given by

$$P_i \propto w_i\, e^{-E_i/k_b T}$$

where w_i is the degeneracy of the system for energy E_i. The proportionality constant is $1/Q$ where

$$Q = \sum_i w_i\, e^{-E_i/k_b T} \tag{19.4}$$

Q is called the *partition function* of the entire system.

$$P_i = \frac{w_i\, e^{-E_i/k_b T}}{\Sigma w_i\, e^{-E_i/k_b T}} = \frac{w_i e^{-E_i/k_b T}}{\Sigma w_i\, e^{-E_i/k_b T}} \tag{19.5}$$

If we know P_i it is possible for us to calculate the average property of the given system at constant T and V. For example, the average energy U is given by

$$U = \Sigma E_i\, P_i = \frac{\Sigma w_i\, E_i\, e^{-E_i/k_b T}}{\Sigma w_i\, e^{-E_i/k_b T}} = k_b T^2 \frac{\Sigma\, w_i\, E_i \frac{1}{k_b\, T^2}\ e^{-E_i/k_b\, T}}{\Sigma w_i\, e^{-E_i/k_b\, T}}$$

$$= k_b\, T^2 \frac{\partial \ln \Sigma\, w_i\, e^{-E_i/k_b\, T}}{\partial\, T} = k_b\, T^2 \frac{\partial \ln Q}{\partial\, T} \tag{19.6}$$

Other properties can be evaluated in a similar manner. These are given in Table 19.1.

TABLE 19.1 *Relations between thermodynamic properties and partition function*

$$U = k_b T^2 \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$A = -k_b T \ln Q$$

$$S = k_b \ln Q + k_b T \left(\frac{\partial \ln Q}{\partial T} \right)$$

$$p = k_b T \left(\frac{\partial \ln Q}{\partial V} \right)$$

$$G = -k_b T \ln Q + kT \left(\frac{\partial \ln Q}{\partial V} \right)$$

$$H = k_b T^2 \left(\frac{\partial \ln Q}{\partial T} \right) + k_b T \left(\frac{\partial \ln Q}{\partial \ln V} \right)$$

$$C_v = k_b T^2 \left(\frac{\delta^2 \ln Q}{\partial T^2} \right) + 2k_b T \left(\frac{\partial \ln Q}{\partial T} \right)$$

19.3 MOLECULAR PARTITION FUNCTION

The energy levels of a system consisting of interacting particles are very difficult to evaluate/determine. Here we shall consider a macroscopic system consisting of non-interacting molecules. This leads to considerable simplification as the partition function Q can be expressed in terms of the molecular partition function q. Let us represent the energy levels of molecules as $\varepsilon_0, \varepsilon_1, \varepsilon_2, \ldots$ with degeneracies $g_0, g_1, g_2 \ldots$, respectively, and the corresponding energy levels and degeneracies for the system be represented by E_0, E_1, E_2 and $w_0, w_1, w_2, \ldots$. Then, the energy of the system is the energies of different molecules, i.e.

$$E_j = \epsilon_1, r + \epsilon_2, s + \ldots \tag{19.7}$$

where E_j is the energy of the system and ϵ_1, r is the energy of molecule 1 in state r, ϵ_2, s is the energy of molecule 2 in state s, and so on.

If the degeneracy of the system is given by Ω_j and those of states $r, s, \ldots$ of the molecules g_r, g_s etc., then

$$\Omega_j = g_r \, g_s \ldots$$

$$\text{then } Q = \sum_j \Omega_j \, e^{-E_j/k_b T} = \sum_g g_r \, g_s \ldots e^{-(\epsilon_1, r + \epsilon_2, s + \ldots)/k_b T}$$

$$= \sum_r g_r \, e^{-\epsilon_1, r/k_b T} \sum_s g_s \, e^{-\epsilon_2, s/k_b T} \ldots$$

$$= q_1 \, q_2 \ldots \tag{19.8}$$

where the molecular partition functions are defined by the equations

$$q_1 = \sum_r g_r \, e^{-\epsilon_1, r/k_b T}$$

$$q_2 = \sum_s g_s \, e^{-\epsilon_2, s/k_b T}$$

where summation over r and s indicate that these have to be carried out over all the energy states of each molecule. If all the molecules happen to be of the same type, Q can be written as

$$Q = q^N \text{ (identical localized non-interacting particles)}$$

$$\text{or } \ln Q = N \ln q \tag{19.9}$$

and $Q = \frac{q^N}{N!}$ (identical non-localized non-interacting particles) (19.10)

or $\ln Q = N \ln Q - N \ln N + N \qquad [\ln N! = N \ln N - N]$

19.4 FACTORIZATION OF MOLECULAR PARTITION FUNCTION

As an approximation, the energy ε_r of a molecule* can be considered as the sum of translational ($\varepsilon_{n,\ \mathrm{tr}}$), rotational ($\varepsilon_{j,\ \mathrm{rot}}$), vibrational ($\varepsilon_{v,\ \mathrm{vib}}$), and electronic ($\varepsilon_{k,\ \mathrm{el}}$) energies

i.e. $$\varepsilon_r = \varepsilon_{n,\ \mathrm{tr}} + \varepsilon_{j\ \mathrm{rot}} + \varepsilon_{v,\ \mathrm{vib}} + \varepsilon_{k,\ \mathrm{el}} \tag{19.11}$$

and also $$g_r = g_n\, g_j\, g_v\, g_k \tag{19.12}$$

Then $$q = \sum_r g_r\, e^{-\varepsilon_r/kT} = \sum_v g_n\, g_j\, g_v\, g_k e^{-(\epsilon_{n,\ \mathrm{tr}} + \epsilon_{j,\ \mathrm{rot}} + \epsilon_{v,\ \mathrm{vib}} + \epsilon_{k,\ \mathrm{el}})/kT}$$

or $$q = \sum_n g_n\, e^{-\epsilon_{n,\ \mathrm{tr}}/kT} \sum_j g_j\, e^{-\varepsilon_{j,\ \mathrm{rot}}/kT} \sum_v g\ e^{-\varepsilon_{v,\ \mathrm{vib}}/kT}$$

$$\sum_k g_k\, e^{-\varepsilon_{k,\ \mathrm{el}}/kT}$$

$$= q_{\mathrm{tr}}\ q_{\mathrm{rot}}\ q_{\mathrm{vib}}\ q_{\mathrm{el}} \tag{19.13}$$

i.e. the molecular partition can be factorized into partition functions due to different degrees of freedom. These, for different types of molecules, are given in Table 19.2.

TABLE 19.2 *Molecular partition function for different degrees of freedom*

	q_{tr}	q_{rot}	q_{vib}	q_{el}
Monoatomic molecules	$\left(\frac{2\pi\, mk_b\, T}{h^2}\right)^{3/2} V$	—	—	$\Sigma g_k\ ^{e - \varepsilon_k,\ \mathrm{el}/k_b T}$
Diatomic molecules	$\left(\frac{2\pi\, mk_b\, T}{h^2}\right)^{3/2} V$	$\frac{8\pi^2\, k_b T}{\sigma\, h^2}$	$(1 - e^{h\nu/k_b T})^{-1}$	$\Sigma g_k\, e^{-\varepsilon_k,\ \mathrm{cl}/k_b T}$
Linear polyatomic molecules	$\left(\frac{2\pi\, mk_b\, T}{h^2}\right)^{3/2} V$	$\frac{8\pi^2\, k_b T}{\sigma\, h^2}$	$\overset{3N-5}{\underset{i}{\pi}} \left(1 - e^{-h\nu_i/k_b T}\right)^{-1}$	$\Sigma\, g_k\, e^{-\varepsilon_k,\ \mathrm{el}/k_b T}$
Non-linear polyatomic molecules	$\left(\frac{2\pi\, mk_b\, T}{h^2}\right)^{3/2} V$	$\frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 k_b T}{h^2}\right)^{3/2} (I_A I_B I_C)^{1/2}$	$\overset{3N-6}{\underset{i}{\pi}} \left(1 - e^{-h\nu_i/k_b T}\right)^{-1}$	$\Sigma\, g_k\ ^{e - \varepsilon_k,\ \mathrm{el}/k_b T}$

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*We are not taking into account the energy of different nuclei as these remain constant in a chemical reaction. However, the nuclear partition function q_{nuc} can be calculated in the usual manner. In statistical mechanics, the lowest energy state is arbitrarily taken as zero. Therefore, different molecules have different zero point references. To this, we also add the zero point vibrational energy ($\Sigma \frac{1}{2} h\nu_i$). The total energy is called the zero point energy ϵ_0 and zero energy partition function $q_{\mathrm{zero}} = e^{-\epsilon_0/k_b T}$.

where m = mass of molecule
h = Planck's constant
V = volume of system
I = moment of inertia of diatomic or linear molecule
σ = symmetry number of a molecule which corresponds to the number of equivalent dispositions of molecules obtained on rotation
I_A, I_B, I_C = moments of inertia around 3 principal axes
ν_i = vibrational frequency of the *i*th normal mode.

Example 19.1 Calculate the following for methane at 300K occupying volume $V = 25\ l\ \text{mol}^{-1}$

(a) $\left(\frac{2\pi\ m\ k_bT}{h^2}\right)^{\frac{1}{2}}$

(b) Translational partition function (molecular)

Solution

(a) For methane molecule, $m = \frac{0.016}{6.02\times 10^{23}}$ kg

$$k_b = 1.38\times 10^{-23}\ \text{J molecule}^{-1}\ \text{deg}^{-1}$$

$$h = 6.62\times 10^{-34}\ \text{J s}$$

Substituting values,

$$\left(\frac{2\pi\ m\ k_bT}{h^2}\right)^{\frac{1}{2}}$$

$$=\left(\frac{2\times 3.14\times \frac{0.016}{6.02\times 10^{23}}\ \text{kg}\times 1.38\times 10^{-23}\ \text{J molecule}^{-1}\times 300\text{K}}{6.02\times 10^{23}\ (6.62\times 10^{-34}\ \text{J s})^2}\right)^{\frac{1}{2}}$$

$$= 3.98\times 10^{10}\frac{1}{\text{m}}$$

(b) Translational partition function

$$q_{tr} = \left(\frac{2\pi\ m\ k_bT}{h^2}\right)^{3/2} V$$

$$V = 25\ l = 25\times 10^{-3}\ \text{m}^3$$

$$\therefore \quad q_{tr} = (3.98\times 10^{10})^3\ \frac{1}{m^3}\ \times(25\times 10^{-3}\ \text{m}^3)$$

$$= 1.58\times 10^{30}$$

Example 19.2 What are the values of σ for I_2, HI, CH_4 and C_6H_6 ?

Solution We have to find how many ways of rotation around each axis gives equal disposition. These are then multiplied.

I_2 = 2
HI = 1
CH_4 = 12
C_6H_6 = 12

Example 19.3 Calculate the rotational and vibrational partition functions of the HBr molecule at 500 K if the internuclear distance is 0.141 nm and the vibration frequency is 265 cm^{-1}. The atomic mass of H and Br may be taken as 0.001 and 0.081 kg mol^{-1}.

Solution

For a diatomic molecule $q_{\text{rot}} = \left(\dfrac{2\pi I\, k_b T}{\sigma h^2}\right)$

Moment of inertia $I = \mu\, r^2$

$$\text{but } \mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\dfrac{0.001}{N_a} \times \dfrac{0.081}{N_a}}{\dfrac{0.082}{N_a}}$$

$$= \frac{0.001 \times 81}{6.02 \times 10^{23} \times 82}$$

$$r = 0.141 \times 10^{-9}\ \text{m} = 1.41 \times 10^{-10}\ \text{m}$$

$$\therefore \quad I = \mu r^2 = \frac{0.001 \times 81}{6.02 \times 10^{23} \times 82} \times (1.41 \times 10^{-10})^2\ \text{kg m}^2$$

$$= \frac{81 \times 1.41 \times 1.41}{6.02 \times 82} \times 10^{-46}$$

$$= 3.27 \times 10^{-47}\ \text{kg m}^2$$

$\sigma = 1$ Putting other values, we obtain

$$q_{\text{rot}} = \frac{2 \times 3.14 \times 3.27 \times 10^{-47} \times 1.38 \times 10^{-23} \times 500}{(6.62 \times 10^{-34})^2}$$

$$= 3.26$$

$$q_{\text{vib}} = \frac{1}{(1 - e^{-h\nu/k_b T})}$$

$$\frac{h\nu}{k_b T} = \frac{6.62 \times 10^{-34} \times 265 \times 3 \times 10^{10}}{1.38 \times 10^{-23} \times 500}$$

$$= \frac{6.62 \times 3 \times 265}{1.38 \times 500} \times 10^{-1}$$

$$= 0.762$$

$$\therefore\ q_{\text{vib}} = \frac{1}{1 - e^{-0.762}} = 1.88$$

Example 19.4 Two electronic energy levels of a molecule have degeneracies 1 and 3 for the ground and excited states respectively. These are 23100 cm^{-1} apart. The ratio of molecules in excited and ground states is 0.003. What is the temperature of the system? What is the electronic partition function with respect to the ground state as reference state, at this temperature and 500K?

Solution $P_1 = \dfrac{g_1\, e^{-\epsilon_1/k_b T}}{Q}$

$$\therefore \quad \frac{P_1}{P_0} = \frac{g_1\, e^{-\epsilon_1/k_b T}}{g_0\, e^{-\epsilon_0/k_b T}}$$

but

$$\frac{n_1}{n_0} = \frac{P_1}{P_0} = \frac{g_1}{g_0}\, e^{-(\epsilon_1 - \epsilon_0)/k_b T}$$

and $\ln\left(\frac{n_1}{n_2} \times \frac{g_0}{g_1}\right) = -\frac{(\varepsilon_1 - \varepsilon_0)}{k_b T}$

$$\varepsilon_1 - \varepsilon_0 = 23100 \times 3 \times 10^{10} \times 6.62 \times 10^{-34}$$
$$= 45.87 \times 10^{-20} \text{ J}$$

$$\therefore \quad \ln(0.003 \times 1/3) = \frac{-45.87 \times 10^{-20}}{T \times 1.38 \times 10^{-23}}$$

or
$$T = \frac{-45.87 \times 10^3}{1.38 \ln(0.001)} = \frac{+45.87}{1.38 \times 6.907} \times 10^3$$
$$= 4812.4 \text{ K}$$

$$q_{el} = g_0\, e^{-\epsilon_0/k_b T} + g_1\, e^{-(\epsilon_1 - \epsilon_0)/k_b T}$$

If ϵ_0 is taken as zero

at $T = 4812.4$ it is already known that the second term is 0.003

$\therefore \quad q_{el} = 1 + 0.003 = 1.003$

At 500°K,

$$q_{el} = g_0\, e^{-\epsilon_0/k_b \times 500} + g_1\, e^{-\frac{(\epsilon_1 - \epsilon_0)}{k_b \times 500}}$$
$$= 1 + 3 \times 10^{-28.8}$$

It can be seen that at a lower temperature, q_{el} is nearly g_0 as contribution from other term is nearly zero especially at lower temperature. For most molecules $g_0 = 1$ and for a large number of molecules $q_{el} \approx 1$.

19.5 THERMODYNAMIC PROPERTIES IN TERMS OF THE MOLECULAR PARTITION FUNCTION

We have already seen that, for an ideal gas consisting of N molecules in a vessel of volume V, at temperature T,

$$Q = \frac{(q_{tr}\, q_{rot}\, q_{vib}\, q_{el})^N}{N!}$$
$$= \left(\frac{q_{tr}}{N e^{-1}}\right)^N (q_{rot}\, q_{vib}\, q_{el})^N \tag{19.14}$$

and
$$\ln Q = N\left\{\ln\left(\frac{q_{tr}\, e}{N}\right) + \ln(q_{rot}) + \ln(q_{vib}) + \ln(q_{el})\right\} \tag{19.15}$$

Each term in the curly bracket is the contribution to ln Q of the molecular partition function corresponding to the different degrees of freedom. The relation between Q and the thermodynamic properties are given in Table 19.1. Expressions for molecular partition functions for different degrees of freedom are given in Table 19.2. These can be substituted and thermodynamic properties can be calculated. However, it can be seen that only q_{tr} depends on V. Therefore, pressure is given by

$$p = k_b T \frac{\partial \ln Q}{\partial V} = N k_b T \frac{\partial \ln \left(q_{\mathrm{tr}} \frac{e}{N} \right)}{\partial V}$$

$$= \frac{N k_b T \, \partial \left[\ln \left\{ \left(\frac{2\pi m k_b T}{h^2} \right)^{3/2} \frac{e}{N} \right\} + \ln V \right]}{\partial V} = \frac{N k_b T}{V} \tag{19.16}$$

Moreover, q_{el} at low temperatures is nearly g_0. For most molecules it is unity. Therefore, $\ln q_{\mathrm{el}}$ is zero. Even if it is equal to g_0, its differential with respect to temperature is zero and hence does not make any contribution to U, C_v and H, but does make a contribution equal to $N k_b \ln g$ to entropy, and hence to A and G also. If, for the molecular ground state, the energy is $U_\circ^\circ$, thermal energy is defined by $U - U_\circ^\circ$.

At absolute zero

$$U_\circ^\circ = A_\circ^\circ \, ; \quad H_\circ^\circ = G_\circ^\circ$$

19.6 CONTRIBUTION BY VARIOUS DEGREES OF FREEDOM TO MOLAR THERMODYNAMIC PROPERTIES OF IDEAL GASES

When N is equal to Avogadro's number, we get the partition function for one mole of an ideal gas from Eq. (19.15). The contributions of each term on the right-hand side, corresponding to the different degrees of freedom, can be calculated.

Translational Degree of Freedom

$$U_{\mathrm{tr}} = \frac{3}{2} RT \tag{19.17}$$

$$S_{\mathrm{tr}} = R \left[\frac{5}{2} \ln T + \frac{3}{2} \ln M - \ln p \right] - 9.68 \text{ J K}^{-1} \text{ mol}^{-1} \tag{19.18}$$

where M is the molar mass in gram and p is in atmospheres. When $p = 1$,

$$S_{\mathrm{tr}} = R \left[\frac{5}{2} \ln T + \frac{3}{2} \ln M \right] - 9.68 \text{ J K}^{-1} \text{ mol}^{-1} \tag{19.19}$$

This is known as the *Sackur–Tetrode equation*

Translational contributions to other properties like H, A, G, etc. can be evaluated using the usual thermodynamic relation and knowing $U_\circ^\circ$.

Rotational Contribution

$$U_{\text{rot}} = RT \quad \text{for diatomic or linear molecules} \tag{19.20}$$

$$= \frac{3}{2} RT \quad \text{for non-linear molecules} \tag{19.21}$$

$$H_{\text{rot}} = U_{\text{rot}}$$

$$S_{\text{rot}} = R\left(1 + \ln \frac{8\pi^2 I\, k_b T}{\sigma\, h^2}\right) \quad \text{for diatomic or linear polyatomic molecules} \tag{19.22}$$

$$= R\left[\frac{3}{2} + \ln\left\{\frac{(\pi I_A I_B I_C)^{1/2}\,(8\,\pi^2\, k_b T)^{3/2}}{h^3}\right\}\right] \quad \text{for polyatomic non-linear molecules} \tag{19.23}$$

Vibrational Contribution

$$U_{\text{vib}} = \sum_{i=1}^{3N-5 \text{ or } 3N-6} \frac{N h\nu_i}{e^{h\nu/k_b T} - 1} \tag{19.24}$$

$$S_{\text{vib}} = R \sum\left[\frac{h\nu_i/k_b T}{e^{h\nu_i/k_b T} - 1} - \ln\left(1 - e^{h\nu_i/k_b T}\right)\right] \tag{19.25}$$

EXAMPLE 19.5 Calculate the translational, rotational and vibrational contributions to molar thermal energy and entropy for $H^{35}Cl$ at 300K and 1 atm, if the following data are available.

$M = 36$ g mol^{-1}, $I = 2.67 \times 10^{-47}$ kg m^2, $\nu = 2888$ cm^{-1}

If $g_0 = 1$, calculate U and S for $H^{35}Cl$

Solution

Translational Contributions

Using Eq. (19.17),

$$U_{\text{tr}} = \frac{3}{2} RT = \frac{3}{2} \times 8.314 \times 300 \text{ J mol}^{-1} = 3714.3 \text{ J mol}^{-1}$$

Using Eq. (19.19),

$$S_{\text{tr}} = R\left[\frac{5}{2} \ln T + \frac{3}{2} \ln M\right] - 9.68 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$= 8.314\left[\frac{5}{2} \ln 300 + \frac{3}{2} \ln 36\right] - 9.68 \text{ J mol}^{-1}\text{ K}^{-1}$$

$$= 153.6 \text{ J mol}^{-1}\text{ K}^{-1}$$

Rotational Contribution

Using Eq. (19.20) for diatomic molecule

$$U_{\text{rot}} = RT = 8.314 \times 300 \quad \text{J mol}^{-1}$$

$$= 2494.2 \text{ J mol}^{-1}$$

Using Eq. (19.21)

$$S_{\text{rot}} = R\left[1 + \ln\left(\frac{8\pi^2\, k_b\, TI}{h^2\, \sigma}\right)\right]$$

$$= R\left(105.54 + \ln \frac{TI}{\sigma}\right)$$

$$= R\left[105.54 + \ln\left(\frac{300 \times 2.67 \times 10^{-47}}{1}\right)\right]$$
$$= 8.318\ (105.54 - 100.67)$$
$$= 40.36\ \text{J mol}^{-1}\ \text{K}^{-1}$$

Vibrational Contribution

$$U_{\text{vib}} = \left(\frac{Nh\nu\ eh\nu/k_b\,T}{1 - e^{-h\nu/k_bT}}\right)$$

$$h\nu = 6.62 \times 10^{-34} \times 2888 \times 3 \times 10^{8} = 5.736 \times 10^{-22}\ \text{J}$$
$$Nh\nu = 34.53 \times 10\ \text{J mol}^{-1} = 345.3\ \text{J mol}^{-1}$$
$$\frac{h\nu}{k_bT} = \frac{5.736 \times 10^{-22}}{1.38 \times 10^{-23} \times 300} = 0.1385$$
$$U_{\text{vib}} = e^{\frac{Nh\nu}{h\nu/k_bT}} - 1 = e^{\frac{345.3}{0.1385}} - 1 = 2324.5\ \text{J mol}^{-1}$$
$$S_{\text{vib}} = R\left[\frac{\frac{h\nu}{k_bT}}{e^{h\nu/k_bT}} - 1\ \ln\left(1 - e^{-h\nu/k_bT}\right)\right]$$
$$= 8.314\left[\left(e^{\frac{0.1385}{0.1385}} - 1\right) - \ln\left(1 - e^{-0.1385}\right)\right]$$
$$= 8.314\ [\,0.93 + 2.052\,] = 24.8\ \text{J mol}^{-1}\ \text{K}^{-1}$$
$$U - U^\circ_\circ = [\,3714.3 + 2494.2 + 2324.5\,]\ \text{J mol}^{-1}$$
$$= 8533\ \text{J mol}^{-1}$$
$$S = 153.6 + 40.4 + 24.8$$
$$= 218\ 8$$

19.7 CALCULATION OF EQUILIBRIUM CONSTANT

For any gaseous reaction

$$aA + bB \rightleftharpoons c\,C$$

the equilibrium constant K_p is related to ΔG° of the reaction, which can be evaluated from the partition functions of the reactant and product molecules. It can be shown that

$$K_p = \left(\frac{k_bT}{p}\right)^{\Delta n}\left(\frac{2\pi\, k_bT}{h^2}\right)^{\Delta n}\left(\frac{m_{\text{C}}^{c}}{m_{\text{A}}^{a}\ m_{\text{B}}^{b}}\right)^{3/2}\left(\frac{q_{\text{rot, C}}^{c}}{q_{\text{rot, A}}^{a} \times q_{\text{rot, B}}^{b}}\right)$$
$$\times\left(\frac{q_{\text{vib, C}}^{c}}{q_{\text{vib, A}}^{a} \times q_{\text{vib, B}}^{b}}\right)\left(\frac{g_{0,\text{C}}^{c}}{g_{0,\text{A}}^{a} \times g_{0,\text{B}}^{b}}\right) \times e^{-\frac{\Delta\varepsilon_0^0}{k_bT}}$$

Where $\Delta n = c - a - b$ and $\Delta\varepsilon_0^0$ is the difference in the zero level of energy, including zero point vibrational energy.

QUESTIONS

Numerical Problems

19.1 Calculate the molecular translational partition function for water at 300°C, its molar volume being 45 *l*. What will be the partition function for 1 mol of water vapour ?

19.2 The bond distance in the OH free radical is 9.6 nm. Calculate its molecular rotational partition function at 300°C.

19.3 The vibrational frequency of a diatomic molecule is 1600 cm^{-1}. Calculate its vibrational partition function at 300, 500 and 1000 K.

19.4 The ground state of the molecule is a singlet whereas its first excited state is a triplet. The energy difference between these is 15,300 cm^{-1}. What will be the ratio of their populations at 500K and what will be the contribution of this excited state to the partition function ?

19.5 The following data are available for CO_2

C-O bond $= 1.15$ A

$\nu_1 = 1330\ cm^{-1}$

$\nu_2 = 2349.3\ cm^{-1}$

$\nu_3(2) = 667.3\ cm^{-1}$

Calculate the rotational and vibrational partition functions at $T = 300$ K

19.6 From the data given in problem (19.5), calculate the rotational and vibrational contributions to entropy and internal energy of one mole of CO_2 at 300 K.

19.7 Using the data in problem (19.5) and the results of problem (19.6), calculate the total partition function for 1 mol of CO_2 at 300 K. Determine its entropy and energy if the electronic ground state is a singlet and the excited states at this temperature are not populated. Assume that the pressure is 1 bar.

19.8 If the bond distance in O_2 is 1.207 Å, its vibrational frequency is 1556.2 cm^{-1} and the ground electronic state is a triplet, calculate the Helmoltz free energy of oxygen per mole at 25°C and 45°C at 1 atmosphere. Hence culculate its entropy and internal energy.

19.9 Using the data in problem (19.8), calculate the molar heat capacity of oxygen at constant volume.

19.10 Using the data in problems (19.5) and (19.8) and the following data for CO:

$$\nu\,(CO) = 2143.3\ cm^{-1},\quad C = O = 1.13\ \text{Å}$$

calculate the equilibrium constant for the reaction

$$2\,CO_2\,(g) \rightleftharpoons 2CO\,(g) + O_2\,(g)$$

at 1000 K.

QUIZ QUESTIONS

Type A: Multiple Choice

19.11 Which of the following has the highest value ?
(a) translational partition function
(b) vibrational partition function
(c) rotational partition function
(d) electronic partition function

19.12 The partition function has the units of
(a) energy
(b) temperature
(c) entropy
(d) a number

19.13 The rotational partition function for a linear molecule depends on
- (a) T, I only
- (b) I, σ only
- (c) σ, T only
- (d) T, I and σ

19.14 The vibrational partition function of a diatomic molecule depends on
- (a) I only
- (b) vibrational frequency ν only
- (c) I and T
- (d) ν and T only

19.15 The translational partition function has the units of
- (a) V
- (b) $1/V$
- (c) p
- (d) a number

Type C: True or False

19.16 The partition function always increases with temperature.

19.17 The ratio of populations of molecules with no energy difference does not change with temperature.

19.18 The bending vibrational frequency generally makes less contribution to the vibrational partition function than the stretching vibrational frequency.

19.19 The symmetry number for the oxygen molecule ($^{16}O\ ^{18}O$) is two.

19.20 The degeneracies of rotational levels increase with the rotational quantum number.

19.21 The translation entropy is less than the vibrational entropy for benzene at room temperature.

19.22 The translational partition function increases with molecular mass.

19.23 The rotational partition function for a linear molecule increases with its moment of inertia.

19.24 The electronic partition function is always one at low temperatures.

19.25 The electronic partition function is g_0 at low temperatures.

Type D: Fill in the Blanks

19.26 The partition function ———— with decrease in temperature.

19.27 The partition function ———— with increase in molecular weight.

19.28 The rotational partition function is ———— than the translational partition function, but ———— than the vibrational partition function.

19.29 The electronic partition function at ———— temperature is generally equal to g_0.

19.30 The rotational partition function is ———— proportional to the symmetry number of the molecule.

19.31 The vibrational partition function at high temperatures reaches the limit ————.

19.32 At low temperatures, the vibrational partition function is nearly ————

19.33 At a given temperature the vibrational partition function ———— with increase in vibrational frequency.

19.34 The largest contribution to entropy is from ———— degree of freedom.

19.35 At very high temperatures, for a large molecule, the vibrational energy is ———— than the translational energy.

ANSWERS

19.1 $q = 8.9\times10^{30}$, $\ln Q = 1.054\times10^{25}$; $Q = e^{1.054\times10^{25}}$ a very large number *19.2* 1.63 *19.3* 1, 1.01 and 1.11 at 300, 500 and 1000 K respectively. *19.4* 2.2×10^{-20} *19.5* $q_{\text{rot}} = 261.8$, $q_{\text{vib}} = 1.0865$ *19.6* $S_{\text{vib}} = 3.75$ J/K mol $E_{\text{vib}} = 705.07$ J/mol $S_{\text{rot}} = 54.58$ J/K mol $E_{\text{rot}} = 2493$ J/mol *19.7* $S = 303.7$ J/K mole $E_{\text{rot}} = 6937.6$ J/mol *19.8* $U_{298} = 6204.3$ J mol^{-1}, $U_{318} = 6625.86$ J mol^{-1}, $S_{298} = 196.4$ J mol^{-1} K^{-1} $S_{318} = 198.5$ J mol^{-1} K^{-1} *19.9* 21.08 J mol^{-1} K^{-1} *19.10* 5.47×10^{-22}.

Quiz Questions

19.11 (a) *19.12* (b) *19.13* (d) *19.14* (d) *19.15* (d) *19.16* True *19.17* True *19.18* False *19.19* False *19.20* True *19.21* False *19.22* True *19.23* True *19.24* False *19.25* True *19.26* Decreases *19.27* increases *19.28* greater, smaller *19.29* 0°K *19.30* inversely *19.31* $\frac{k_bT}{h\nu}$ *19.32* unity *19.33* decreases *19.34* translational *19.35* greater.

20

Kinetics and Catalysis

Chemical kinetics is concerned with the measurement and interpretation of reactions and the influence of the factors (temperature, pressure, concentration, etc.) on the reaction rates. The study of chemical kinetics helps in the elucidation of reaction mechanisms and development of new chemical processes which can give a good yield of the desired products in the minimum possible time.

20.1 RATE OF A CHEMICAL REACTION

The rate of a reaction may be expressed as the rate of change of concentration of any reactant or product of the reaction. For a reaction of the type

$$A + B \longrightarrow P$$

the rate may be expressed either by the rate of formation of the product or the rate of disappearance of any of the reactants, i.e.

$$\text{Rate of the reaction} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} \qquad (20.1)$$

The negative sign in case of reactants A and B implies that the concentration of the reactants is decreasing and the rate becomes positive in either case.

For a general reaction,

$$aA + bB \longrightarrow lL + mM$$

it has been agreed, by convention, to define the rate of reaction by

$$-\frac{1}{a}\,\frac{d[A]}{dt} = -\frac{1}{b}\,\frac{d[B]}{dt} = \frac{1}{l}\,\frac{d[L]}{dt} = \frac{1}{m}\,\frac{d[M]}{dt} \qquad (20.2)$$

20.2 ELEMENTARY AND COMPLEX REACTIONS

Most reactions do not occur in one step but take place in a sequence of steps, involving the reactant and reactive intermediates, to finally give the products. Such reactions, which take place through a sequence of two or more steps, are called *complex reactions*. The various steps or reactions which contribute to the overall reaction are called *elementary processes* or *elementary reactions.*

The degree of complexity of the reaction or the number and nature of the elementary reactions depend upon the reacting system itself.

20.3 FACTORS INFLUENCING RATES OF REACTIONS

Some important factors which influence rates of reactions are:

(a) Concentration of the reactants
(b) Temperature of the system
(c) Pressure over the reacting system
(d) Nature of reactants and products
(e) Presence of external agents like (i) inert substances (ii) catalysts (iii) radiations, etc.

20.4 RATE AND ITS DEPENDENCE ON THE CONCENTRATION OF THE REACTANTS

In general, the rate of a reaction of the type

$$aA + bB + \ldots \longrightarrow lL + mM + \ldots$$

is given by the equation

$$\text{Rate} = f(C_A, C_B, \ldots) \tag{20.3}$$

where f is the mathematical function of $C_A, C_B, \ldots$ which are the concentrations of the various reactants in the system. However, from the kinetic study of the reaction, the dependence of concentration of reactants on the rate of many reactions has been found to be

$$\text{Rate} = k\, C_A{}^{n_A}\, C_B{}^{n_B} \ldots \tag{20.4}$$

where k is a proportionality constant known as the rate constant and $n_A, n_B, \ldots$ are the powers of the concentrations of reactants A, B, ... on which the rate of the reaction depends. Expression 20.4 is also known as the *rate law equation.*

20.5 MOLECULARITY AND ORDER OF A REACTION

Molecularity is the number of reacting species (molecules, atoms or ions) which collide simultaneously to bring about a chemical reaction in an elementary reaction. If the reaction involves the decomposition of a single species, it is called unimolecular, e.g.

$$\text{Cyclo propane} \longrightarrow \text{propane}$$

Similarly, the bimolecular and termolecular reactions are:

bimolecular : $2HI\,(g) \longrightarrow H_2\,(g) + I_2\,(g)$
termolecular : $2CH_3\cdot + M \longrightarrow C_2H_6 + M$

where M is any molecule acting as a third body.

It may be noted that reactions involving a molecularity of three or more are uncommon. This is because such reactions require the simultaneous collision of three or more molecules, which is rare. However, it has been observed that some reactions involving three or more molecules are quite fast. Such reactions do not occur in one step, but in a sequence of two or more consecutive steps (called complex reactions). The detailed description of the various steps (elementary reactions) by which reactants change into products is called the mechanism of the reaction.

In such reactions, the overall chemical reaction does not provide any clue to the number of molecules colliding (except in single step reactions). Hence, molecularity has no meaning for the overall reaction. It is concerned with each elementary step or reaction which proceeds through one step only.

Order of a Reaction

If the rate of a reaction is directly proportional to n_A power of the concentration of 'A' and n_B power of the concentration of 'B' (as expressed in Eq. 20.4), the reaction is n_A order in A and n_B order in B. The overall order of the reaction is $n_A + n_B$. In general, the reaction order with respect to a particular substance is the exponent of the concentration in the rate equation. The overall order is the sum of all exponents. Thus, if rate of a reaction

$$aA + bB + cC + \ldots \longrightarrow \text{Products}$$

is Rate $= k\,[A]^{n_A}\,[B]^{n_B}\,[C]^{n_C}\ldots$

Then, order n of the reaction is $n_A + n_B + n_C + \ldots$

It may be noted that there is no relation between the stoichiometric coefficients a, b, c and the order wrt of the reactants n_A, n_B, n_C, . . . for a complex reaction. Further, it is not necessary that n_A, n_B, . . . are whole numbers, these can be fractions as well. For example, the order for the decomposition of acetaldehyde into methane and carbon monoxide is 1.5. The order of a reaction has always to be measured experimentally. In certain cases, the rates of the reactions and concentrations cannot be expressed by a simple relationship (as Eq. 20.5) as the relationship is very complicated. As a result, the order of such reactions cannot be defined.

EXAMPLE 20.1 (a) Write the differential rate equations for the following single-step reactions:

(i) $2NO_2\,(g) \longrightarrow 2NO\,(g) + O_2\,(g)$

(ii) $A + 2B + C \longrightarrow 3D + 2E$ (hypothetical)

(b) The reaction $A \longrightarrow B$ has been found to be second order with respect to A.

(i) Write the rate expression for this reaction.

(ii) What are the units of its rate constant if the concentrations are expressed as mol dm^{-3} and time in seconds.

Solution (a) The differential rate equations:

(i) $$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{1}{2}\frac{d[NO]}{dt} = \frac{d[O_2]}{dt} = k[NO_2]^2$$

(ii) $$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = -\frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt} = \frac{1}{2}\frac{d[E]}{dt} = k[A][B]^2[C]$$

(b) (i) For the reaction $A \rightarrow B$, order has been found to be 2. Therefore, rate depends upon the square of the concentration of A. Thus,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^2$$

(ii) Now, rate is the change in concentration with time, expressed in terms of mol dm^{-3} s^{-1}, and concentration of A is mol dm^{-3}. This means,

$$\text{mol dm}^{-3}\text{ s}^{-1} = k(\text{mol dm}^{-3})^2$$

or $$k = \text{mol}^{-1}\text{ dm}^3\text{ s}^{-1}$$

20.6 INTEGRATED RATE EQUATIONS FOR DIFFERENT ORDER REACTIONS

Zero Order Reaction

In this case, the rate of the reaction is independent of the concentration of any reactant in the system

$$\text{Rate} = -\frac{dC}{dt} = k(C)^0 = k$$

The concentration of the reactant C at any time t is given by

$$C = C_0 - kt$$

or $$k = \frac{C_0 - C}{t}$$

While C_0 is the initial concentration.

First Order Reaction

For the reaction $A \longrightarrow$ Products

$$\text{Rate} = -\frac{dC_A}{dt} = k\,C_A \text{ and } k = \frac{2.303}{t}\log\frac{C_A{}^0}{C_A} \tag{20.5}$$

$$\text{and } C_A = C_{A_0}\,e^{-kt} \tag{20.6}$$

If at $t = 0$, concentration of A, $C_{A0} = a$, and at time t, concentration of A, $C_A = (a - x)$, then

$$k = \frac{2.303}{t}\log\frac{a}{(a-x)} \tag{20.7}$$

Second Order Reaction

For the reaction

$$2A \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{dC_A}{dt} = kC_A^2 \text{ and } k = \frac{1}{t}\left[\frac{1}{C} - \frac{1}{C_0}\right] \tag{20.8}$$

If at $t = 0$, concentration of A, $C_{A0} = a$; and at time t, concentration of A, $C_A = (a-x)$, then

$$k = \frac{1}{t}\left[\frac{x}{a(a-x)}\right] \tag{20.9}$$

For the second order reaction of the type

$$A + B \longrightarrow \text{Products}$$

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B$$

and
$$k = \frac{1}{t[C_{A0} - C_{B0}]} \ln \frac{C_A C_{B0}}{C_{A0} C_B} \tag{20.10}$$

or
$$k = \frac{1}{t(b-a)} \ln \left\{\frac{a(b-x)}{b(a-x)}\right\} \tag{20.11}$$

where a and b are the initial concentrations of A and B, respectively.

Third Order Reaction

For the reaction

$$3A \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{dC_A}{dt} = kC_A^3 \text{ and } k = \frac{1}{2t}\left[\frac{1}{C_A^2} - \frac{1}{C_{A_0}^2}\right] \tag{20.12}$$

***n*th Order ($n \geqslant 2$) Reaction**

For the reaction

$$A \longrightarrow \text{Products}$$

$$\text{Rate} = -\frac{dC_A}{dt} = kC_A^n$$

and
$$k = \frac{1}{t(n-1)}\left[\frac{1}{C_A^{\,n-1}} - \frac{1}{C_{A_0}^{\,n-1}}\right] \tag{20.13}$$

EXAMPLE 20.2 The rate constant of a zero order reaction is 0.2 mol dm^{-3} h^{-1}. What will be the initial concentration of the reactant if, after half an hour, its concentration is 0.05 mol dm^{-3} ?

Solution The concentration of the reactant (C) after time t is given by

$$C = C_0 - kt$$

$$C = 0.05, \quad k = 0.2 \text{ mol dm}^{-3} \text{ h}^{-1}, \quad t = \tfrac{1}{2} \text{ h}$$

The initial concentration, C_0 is given as

$$C_0 = C + kt = 0.05 + 0.2 \times \tfrac{1}{2}$$
$$= 0.15 \text{ mol dm}^{-3}$$

EXAMPLE 20.3 The decomposition of hydrogen peroxide into water and oxygen has been found to be of the first order. The kinetics can be followed by estimating the concentration of H_2O_2 by titrating against standard $KMnO_4$.

The following data have been obtained.

Time (min)	0	20	30	40	50	60	70
Conc. of H_2O_2 (mol l^{-1})	0.1297	0.1077	0.09672	0.08482	0.07830	0.07076	0.06145

Calculate the value of the rate constant.

Solution The value of k can be calculated from the relation

$$k = \frac{2.303}{t}\left[\log a - \log(a-x)\right]$$

Time (min)	Conc. of H_2O_2 $(a-x)$	k
0	0.12970	—
20	0.10770	0.0093
30	0.09672	0.0099
40	0.08482	0.0106
50	0.07830	0.0101
60	0.07076	0.0101
70	0.06145	0.0107

The value of k is almost constant and the mean value is 0.0101 min^{-1}.

The value of k can also be calculated by drawing a graph between $\log(a-x)$ and t. The slope has been found to be (Fig. 20.1) equal to -4.4×10^{-3} and

$$k = -2.303\times\text{slope}$$
$$= -2.303\times(-4.4\times10^{-3})$$
$$= 0.0101\ \text{min}^{-1}$$

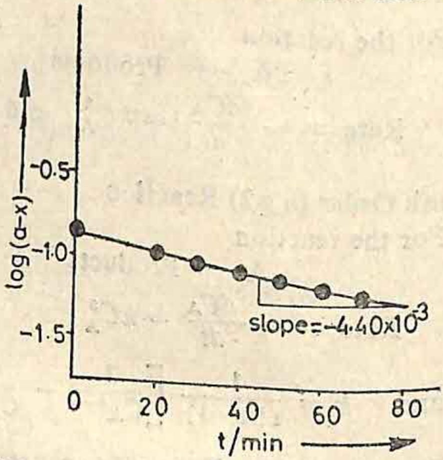


FIG. 20.1 *Graph between log (a−x) and t*

Example 20.4 (SI Units) Crowell and Hammett studied the kinetics of the following reaction at 310.5 K.

$$n\ C_3H_7Br + S_2O_3^{2-} \longrightarrow n\ C_3H_7S_2O_3^- + Br^-$$

The reaction was found to be of second order. They followed the reaction by the titration of the free thiosulphate ion against iodine solution and obtained the following data:

Time(s)	0	1110	2010	3192	5052	7380
Conc. of $S_2O_3^{2-}$ (mol dm^{-3})	0.0966	0.0904	0.0863	0.0819	0.0766	0.072

Determine the rate constant if the initial concentration of n-C_3H_7Br is 0.0395 mol dm^{-3}.

Solution For a second order reaction, the rate constant is given as

$$k = \frac{1 \times 2.303}{t\,(a-b)} \log \frac{b\,(a-x)}{a\,(b-x)} = \frac{2.303}{t\,(a-x)} \left[\log \frac{b}{a} + \log \frac{a-x}{b-x} \right]$$

Let the concentration of the $S_2O_3^{2-}$ ion $= a-x$

Initial concentration of $S_2O_3^{2-}$ ion $= a = 0.0966$ mol dm^{-3}.

$$\therefore \quad x = a-(a-x)$$

The initial concentration of n-C_3H_7Br $= b = 0.0395$

$(b-x)$ can be determined at different times. Substituting in the above relation, k can be calculated.

Time (s)	Conc. of $S_2O_3^{2-}$ mol dm^{-3} $(a-x)$	x mol dm^{-3}	Conc. of C_3H_7Br $(b-x)$ mol dm^{-3}	k mol^{-1} dm^3 s^{-1}
0	0.0966	0.0000	0.0395	—
1110	0.0904	0.0062	0.0333	0.001653
2010	0.0863	0.0103	0.0292	0.001649
3192	0.0819	0.0147	0.0248	0.001649
5052	0.0766	0.0200	0.0196	0.001626
7380	0.0720	0.0246	0.0149	0.001617

Mean value of rate constant $= 1.64 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}

Alternatively, the above equation may be written as

$$\log \frac{a-x}{b-x} = \log \frac{a}{b} + \frac{k\,(a-b)}{2.303}\,t$$

A graph (Fig. 20.2) is drawn between $\log \dfrac{a-x}{b-x}$ and t so that slope $= \dfrac{k\,(a-b)}{2.303}$. The slope of the graph is 0.4071×10^{-4} so that

$$k = \frac{2.303}{(a-b)} \times \text{slope}$$

$$= \frac{2.303}{0.0571} \times 0.4071 \times 10^{-4}$$

$$= 1.64 \times 10^{-3} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$$

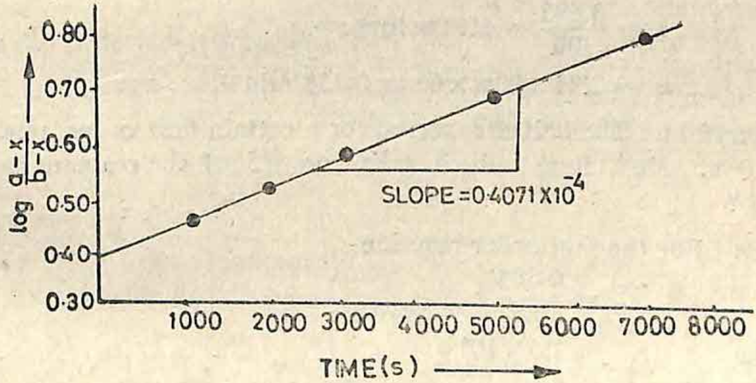


FIG. 20.2 *Graph of log* $\dfrac{a-x}{b-x}$ *and t*

20.7 FRACTIONAL LIFE PERIOD—Half Life Period

Fractional life period is the time taken to reduce the concentration of the reactants to any fraction of the initial concentration. For example, the *half life period* stands for the time taken to reduce the concentration of the reactants to one half, and is expressed as $t_{\frac{1}{2}}$. When one half of the reactant has been used up, $a-x = a/2$.

For the first order reaction, substituting $a-x = a/2$ in Eq. (20.7)

$$t_{\frac{1}{2}} = \frac{2.303}{k} \log 2 = \frac{0.693}{k} \tag{20.14}$$

Thus, the half life period for the first order reaction is independent of the initial concentration.

For a second order reaction, using Eq. (20.9),

$$t_{\frac{1}{2}} = \frac{1}{kC_{A0}} \tag{20.15}$$

Similarly for a third order reaction

$$t_{\frac{1}{2}} = \frac{3}{2k\,(C_{A0})^2} \tag{20.16}$$

and for the *n*th order reaction

$$t_{\frac{1}{2}} = \frac{2^{n-1}-1}{(n-1)\,k(C_{A0})^{n-1}} \tag{20.17}$$

EXAMPLE 20.5 The half-life period of a reaction of the first order is 300 s. Calculate its rate constant in seconds and minutes.

Solution For a first-order reaction

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$\therefore\ k = \frac{0.693}{t_{\frac{1}{2}}}$$

$$t_{\frac{1}{2}} = 300 \text{ s}$$

$$k = \frac{0.693}{300} = 2.31\times 10^{-3}\ \text{s}^{-1}$$

and $$k = 2.31\times 10^{-3}\times 60 = 0.138\ \text{min}^{-1}$$

EXAMPLE 20.6 The half-life period for a certain first order reaction is 2.5×10^3 s. How long will it take for 1/5 of the reactant to be left behind ?

Solution For the first order reaction,

$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

Now $$t_{\frac{1}{2}} = 2.5\times 10^3 \text{ s}$$

$$k = \frac{0.693}{2.5\times 10^3} = 2.77\times 10^{-4}\ \text{s}^{-1}$$

Let the time taken for the reactant to decrease in concentration to 1/5 be t'. Then,

$$a = 1 \quad \text{(say)}$$

and $(a-x) = 1/5$

so that
$$t' = \frac{2.303}{k} \log \frac{a}{a-x}$$
$$= \frac{2.303}{2.77 \times 10^{-4}} \log \frac{1}{1/5}$$
$$= 5.8 \times 10^3 \text{ s}$$

EXAMPLE 20.7 A reaction is second order in one of the reactants and the rate constant is 0.5 $\text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}$. What is the half-life period if the initial concentration is (i) 0.2 mol dm^{-3} and (ii) 0.1 mol dm^{-3}.

Solution For a second order reaction,

$$t_{\frac{1}{2}} = \frac{1}{ka}$$

$k = 0.5$ and (i) $a = 0.2 \text{ mol dm}^{-3}$

$$t_{\frac{1}{2}} = \frac{1}{0.5 \text{ mol}^{-1}\text{ dm}^3\text{ min}^{-1} \times 0.2 \text{ mol dm}^{-3}}$$
$$= 10 \text{ min}$$

(ii) when $a = 0.1 \text{ mol dm}^{-3}$

$$t_{\frac{1}{2}} = \frac{1}{(0.5 \text{ mol}^{-1}\text{ dm}^3\text{ min}^{-1}) \times (0.1 \text{ mol dm}^{-3})}$$
$$= 20 \text{ min}$$

20.8 METHODS OF DETERMINATION OF ORDER OF A REACTION

The following are the methods for the determination of the order of a reaction:

From the Differential Rate Equation

If r_1 and r_2 are the rates of reactions at concentrations C_1 and C_2 of a reactant, while other factors such as concentration of the other reactants and temperature are constant,

$$\frac{r_1}{r_2} = \left(\frac{C_1}{C_2}\right)^n \tag{20.18}$$

where n is the order of the reaction with respect to the reactant under consideration. This may also be expressed as

$$n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2} \tag{20.19}$$

From the Integral Rate Equation or Hit and Trial Method

This can be done in two ways:

Graphical Method

In this method, an appropriate function of the concentration is plotted against time. The resulting curve will be a straight line only for the case in which the appropriate integrated equation has been used.

Analytical Method

In this method, the value of k may be calculated by using different integrated rate equations (refer 20.5) at different times. Only one such equation will give a constant value of k. The order of the reaction will correspond to the order of reaction for that integrated equation. This is a hit-and-trial method and one must try different equations before finally getting the correct answer.

Half-life Method

This method is based on the principle that if a reaction is of the nth order in a reactant, the half-life period is inversely proportional to the $(n-1)$th power of its initial concentration, i.e.

$$t_{\frac{1}{2}} \propto \frac{1}{C_0^{n-1}}$$

Thus, if the half-life periods corresponding to different initial concentrations are known,

$$\frac{t_{\frac{1}{2}}'}{t_{\frac{1}{2}}''} = \left(\frac{C_0''}{C_0'}\right)^{n-1}$$

or

$$n = \frac{\log (t_{\frac{1}{2}}'/t_{\frac{1}{2}}'')}{\log (C_0''/C_0')} + 1$$

This method can be generalized to any fractional life time and the equation can be used as such.

Method of Isolation (Van't Hoff)

This method is used to find the order of a reaction with respect to one reactant at a time. The total order of the reaction is then equal to the sum of the orders of reactions for individual reactants. This method is based on the principle that if the concentrations of all but one reactant are taken in excess, then, during the course of the reaction, the concentration of those reactants taken in excess will remain almost constant and hence variation in rate will correspond to the concentration of that reactant whose concentration is small.

EXAMPLE 20.8 (SI Units) The rate of a reaction at concentrations 0.15 mol dm^{-3} and 0.05 mol dm^{-3} are 2.7×10^{-3} and 0.3×10^{-3} mol dm^{-3} min^{-1}. What is the order of the reaction with respect to the reactant ?

Solution Order of the reaction,

$$n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2} = \frac{\log \dfrac{r_1}{r_2}}{\log \dfrac{C_1}{C_2}}$$

$$r_1 = 2.7\times10^{-7} \text{ mol dm}^{-3}\text{ min}^{-1},\quad r_2 = 0.3\times10^{-3} \text{ mol dm}^{-3}\text{ min}^{-1}$$
$$C_1 = 0.15 \text{ mol dm}^{-3},\quad C_2 = 0.05 \text{ mol dm}^{-3}$$

$$n = \frac{\log \dfrac{2.7\times10^{-3}}{0.3\times10^{-3}}}{\log\left(\dfrac{0.15}{0.05}\right)} = \frac{\log 9}{\log 3} = \frac{0.9542}{0.4771} = 2$$

Example 20.9 The half-life time for the conversion of ammonium cyanate into urea at 303 K, at initial concentrations of ammonium cyanate of 0.1 mol dm^{-3} and 0.2 mol dm^{-3}, are 1152 min and 568 min, respectively. What is the order of the reaction ?

Solution In terms of half-life times at different concentrations, the order of the reaction,

$$n = \frac{\log \dfrac{t_{\frac{1}{2}}'}{t_{\frac{1}{2}}''}}{\log \dfrac{C_0''}{C_0'}} + 1$$

$$t_{\frac{1}{2}}' = 1152 \text{ min},\ C_0' = 0.1 \text{ mol dm}^{-3}$$

$$t_{\frac{1}{2}}'' = 586 \text{ min},\ C_0'' = 0.2 \text{ mol dm}^{-3}$$

$$n = \frac{\log 1152/568}{\log 0.2/0.1} + 1 = \frac{0.3071}{0.3010} + 1$$
$$= 1.02 + 1 = 2.02$$

Thus, the order of the reaction is 2.

Example 20.10 Determine the order of reaction from the following data

Conc. of A (mol dm^{-3})	1.00	1.00	0.02	0.04
Conc. of B (mol dm^{-3})	0.02	0.04	1.00	1.00
Rate of reaction (mol dm^{-3} min^{-1})	4.6×10^{-4}	9.2×10^{-4}	9.2×10^{-6}	3.68×10^{-5}

Determine the true rate constant also.

Solution When the concentration of A is very large and constant, the rate depends on the concentration of B only. Therefore, n_B (the order of the reaction with respect to B) is calculated from the relation,

$$n_B = \frac{\log r_1/r_2}{\log C_1/C_2}$$

$$r_1 = 4.6\times10^{-4} \text{ mol dm}^{-3}\text{ min}^{-1},\quad C_1 = 0.02 \text{ mol dm}^{-3}$$
$$r_2 = 9.2\times10^{-4} \text{ mol dm}^{-3}\text{ min}^{-1},\quad C_2 = 0.04 \text{ mol dm}^{-3}$$

$$\therefore \quad n_B = \frac{\log \dfrac{4.6\times10^{-4}}{9.2\times10^{-4}}}{\log \dfrac{0.02}{0.04}} = \frac{-0.301}{-0.301} = 1$$

When the concentration of B is very large and constant, the rate depends on the concentration of A, so that

$$n_A = \frac{\log r_1'/r_2'}{\log C_1'/C_2'}$$

$$r_1' = 9.2\times10^{-6}\ \text{mol dm}^{-3}\ \text{min}^{-1}. \quad C_1' = 0.02\ \text{mol dm}^{-3}$$
$$r_2' = 3.68\times10^{-5}\ \text{mol dm}^{-3}\ \text{min}^{-1}, \quad C_2' = 0.04\ \text{mol dm}^{-3}$$

$$\therefore \quad n_A = \frac{\log \dfrac{9.2\times10^{-6}}{3.68\times10^{-5}}}{\log \dfrac{0.02}{0.04}} = \frac{-0.602}{-0.301} = 2$$

Therefore, the order of the reaction $n = n_A + n_B$
$= 2 + 1 = 3$

The rate expression may be written as

$$\text{Rate} = k\, C_A^2\, C_B$$

and the true rate constant, $k = \dfrac{\text{Rate}}{C_A^2\, C_B}$

This may be calculated as

(I) $k = \dfrac{4.6\times10^{-4}}{(1.00)^2\,(0.02)} = 2.3\times10^{-2}\ \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$

(II) $k = \dfrac{9.2\times10^{-4}}{(1.00)^2\,(0.04)} = 2.3\times10^{-2}\ \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$

(III) $k = \dfrac{9.2\times10^{-6}}{(0.02)^2\,(1.00)} = 2.3\times10^{-2}\ \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$

(IV) $k = \dfrac{3.68\times10^{-5}}{(0.04)^2\,(1.00)} = 2.3\times10^{-2}\ \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$

Thus, the true rate constant $= 2.3\times10^{-2}\ \text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$

20.9 TEMPERATURE DEPENDENCE OF RATE OF A REACTION

According to Arrhenius' law,

$$k = A\, e^{-E_a/RT}$$

or $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where A is the frequency factor, E_a is the activation energy and k_1 and k_2 are the rate constants at T_1 and T_2.

EXAMPLE 20.11 The rate constants of a reaction at 27°C and 37°C are $1.3\times10^{-3}\ \text{s}^{-1}$ and $2.6\times10^{-3}\ \text{s}^{-1}$, respectively. Determine its activation energy and the frequency factor.

Solution According to Arrhenius' law,

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\, R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or $$E_a = \frac{2.303\ R\ (\log k_2/k_1)\ T_1\ T_2}{T_2 - T_1}$$

$$k_1 = 1.3 \times 10^{-3}\ \text{s}^{-1}, \qquad k_2 = 2.6 \times 10^{-3}\ \text{s}^{-1}$$

$$T_1 = 273 + 27 = 300\ \text{K}, \quad T_2 = 273 + 37 = 310\ \text{K}$$

$$E_a = \frac{2.303 \times 8.314 \times \left(\log \dfrac{2.6 \times 10^{-3}}{1.3 \times 10^{-3}}\right) \times 310 \times 300}{310 \times 300}$$

$$= 53.6\ \text{kJ mol}^{-1}$$

Now, $k = A\,e^{-E_a/RT}$

or $$\log k = \log A - \frac{E_a}{RT} \text{ or } \log A = \log k + \frac{E_a}{RT}$$

$$\log A = \log 1.3 \times 10^{-3} + \frac{53.6 \times 10^3}{2\ 303 \times 8.314 \times 300}$$

$$= \bar{3}.1139 + 9.3312$$

$$= 6.4451$$

or $$A = 2.787 \times 10^6\ \text{s}^{-1}$$

EXAMPLE 20.12 The following data have been obtained for the rate constant of the decomposition of a compound in the gas phase:

T (K)	700	730	760	790	820	850
k (mol^{-1} dm^3 s^{-1})	0.016	0.038	0.108	0.352	0.79	2.2

Calculate the value of the activation energy for the reaction.

Solution The Arrhenius' equation is

$$\log k = \log A - \frac{E_a}{2.303\ RT}$$

The plot of $\log k$ vs $\frac{1}{T}$ should give a straight line

$\log k$	-1.796	-1.420	-0.966	-0.453	-0.102	0.342
$\frac{1}{T}$	1.43×10^{-3}	1.36×10^{-3}	1.32×10^{-3}	1.27×10^{-3}	1.22×10^{-3}	1.18×10^{-3}

A plot of $\log k$ vs $1/T$ is shown in Fig. 20.3. The slope has been found to be -9860.

Now slope $= -\dfrac{E_a}{2.303\ R}$

or $$E_a = --2.303 \times 8.314 \times (\text{slope})$$

$$= -2.303 \times 8.314(-9860)$$

$$= 188.8\ \text{kJ mol}^{-1}$$

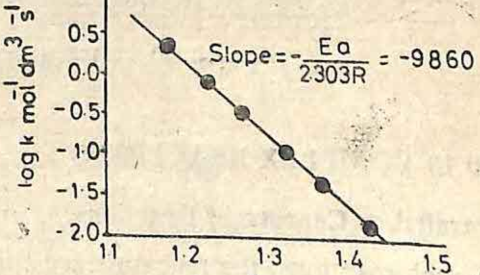


FIG. 20.3 *Plot of log k vs I/T for reaction*

EXAMPLE 20.13 The activation energy for the decomposition of N_2O_5 is 103 kJ mol^{-1}.

(a) What will be the ratio of their rates at 0°C and 25°C (the rates being measured at the same concentration of reactants)?

(b) If the rate constant of the reaction at 25°C is 2×10^{-3} min^{-1}, calculate the rate constant for the reaction at 0°C and 50°C.

Solution Let k_1 and k_2 be the rate constants for the decomposition of N_2O_5 at T_1 (273 K) and T_2 (298 K), respectively. According to Arrhenius' law,

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$E_a = 103\text{ kJ},\quad R = 8.314\text{ J K}^{-1}\text{ mol}^{-1}$$

(a) $$\log\frac{k_2}{k_1}=\frac{103\times 10^3}{2.303\times 8.314}\left[\frac{1}{273}-\frac{1}{298}\right]$$

$$= 1.653$$

or $$\frac{k_2}{k_1}= 45$$

Since the concentrations are the same,

$$\frac{r_2}{r_1}=\frac{k_2}{k_1}=45$$

(b) Arrhenius' law,

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303\,R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

$$T_1 = 273+25 = 298\text{ K},\quad k_1 = 2\times 10^{-3}\text{ min}^{-1}$$

$$T_2 = 273\text{ K},\quad k_2 = ?$$

$$\log\frac{k_2}{2\times 10^{-3}}=\frac{103\times 10^3}{2.303\times 8.314}\left[\frac{1}{298}-\frac{1}{273}\right]$$

$$\frac{k_2}{2\times 10^{-3}}=0.0223$$

$$k_2 = 4.45\times 10^{-5}\text{ min}^{-1}$$

Similarly, at $T_2 = 273+50 = 323$ K, $k_2 = ?$

$$T_1 = 298\text{ K},\quad k_1 = 2\times 10^{-3}\text{ min}^{-1}$$

$$\log\frac{k_2}{2\times 10^{-3}}=\frac{103\times 10^3}{2.303\times 8.314}\left[\frac{1}{298}-\frac{1}{323}\right]$$

$$= 1.397$$

or $$\frac{k_2}{2\times 10^{-3}}=24.946$$

$$k_2 = 4.99\times 10^{-2}\text{ min}^{-1}$$

20.10 COMPLEX REACTIONS

Parallel or Concurrent Reactions

In such reactions, the reactants are consumed by two or more reactions, which may have different orders of reactions, taking place simultaneously. For example, in a system containing NO_2 and SO_2, NO_2 is consumed in the following two reactions:

$$2NO_2 \xrightarrow{k_1} N_2O_4$$

$$NO_2 + SO_2 \xrightarrow{k_2} NO + SO_3$$

The rate of disappearance of NO_2 will be the sum of the rates of the two reactions, i.e.

$$\frac{-d\,[NO_2]}{dt} = 2k_1\,[NO_2]^2 + k_2\,[NO_2]\,[SO_3]$$

Consecutive Reactions

In such reactions, the reactants form a stable intermediate compound before they are finally converted into the products. For example, A is first converted into B and then B is converted to C as

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

In these reactions, each stage will have its own rate and rate constant. If we start with pure A, the concentration of A will always decrease, while the concentration of B will first increase and then decrease, passing through a maximum. The concentration of C will always increase.

Reversible Reactions

In such reactions, products start reacting to give back the reactants. For example, in the reaction

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

The rate of disappearance of NO_2 is

$$-\frac{d\,[NO_2]}{dt} = 2k_1\,[NO_2]^2 - k_2\,[N_2O_4]$$

The rate constants k_1 and k_2 can be determined if the equilibrium constant is known.

Chain Reactions

These reactions proceed in a number of steps and involve reactive species (like atoms or free radicals) before the final products are formed. For example, the decomposition of acetaldehyde

$$CH_3CHO \longrightarrow CH_4 + CO$$

has the following steps:

Chain initiation $CH_3CHO \longrightarrow \dot{C}H_3 + \dot{C}HO$

Chain propagation $\dot{C}H_3 + CH_3CHO \longrightarrow CH_4 + CH_3\dot{C}O$

$$CH_3\dot{C}O \longrightarrow \dot{C}H_3 + CO$$

Chain termination $\dot{C}H_3 + \dot{C}H_3 \longrightarrow C_2H_6$

The rate of the reaction has been found to be

$$\text{Rate} = k\,[\mathrm{CH_3CHO}]^{3/2}$$

This can be derived from the steady state hypothesis.

20.11 THEORIES OF REACTION RATES

Transition State Theory

According to this, the reactants are first converted into an activated complex which is assumed to be in equilibrium with the reactants. The activated complex has only a transient existence and has the attributes of a normal molecule, except for one of the vibrational degrees being converted into translational along the reaction coordinate leading to the formation of the products. The energy variation along the reaction path is shown in Fig. 20.4.

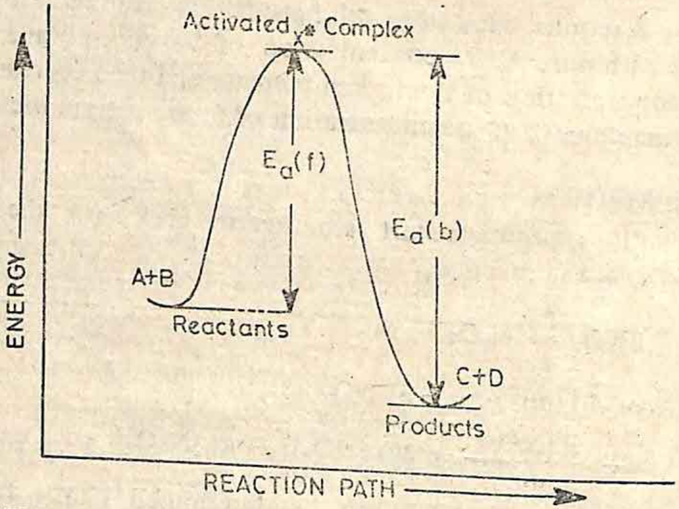


FIG. 20.4 *Energy variation along the reaction path in the activated complex theory*

According to this theory, reactants A and B are first converted into the activated complex (X)*. The process may be written as

$$\mathrm{A + B \rightleftharpoons X^* \longrightarrow C + D}$$

According to this theory,

$$k = \frac{k_b T}{h}\, e^{\Delta S^*/R}\; e^{-\Delta H^*/RT}$$

or

$$k = \frac{k_b T}{h}\, e^{-\Delta G^*/RT}$$

where ΔG^*, ΔH^* and ΔS^* are the free energy, enthalpy and entropy of activation, k_b is the Boltzmann constant and h is Planck's constant.

The enthalpies for the forward and backward reactions are related to enthalpy of reaction as

$$\Delta H = \Delta H^* \text{ (forward)} - \Delta H^* \text{ (backward)}$$

For a gaseous reactions, ΔH^* and Arrhenius activation energy E_a are related by the equation

$$\Delta H^* = E_a - nRT$$

where n is the molecularity of the reaction.

For a reaction in solution or in the liquid state,

$$\Delta H^* = E_a - RT$$

Collision Theory

According to this, molecules react on collision but only those collisions in which the colliding molecules possess a certain minimum amount of energy are effective. According to this theory,

$$k = p\,Ze^{-E_a/RT}$$

where $Z = \pi\left(\dfrac{\sigma_A + \sigma_B}{2}\right)^2 \sqrt{\dfrac{8k_bT}{\pi\, m_A\, m_B}}$, σ_A and σ_B are the diameters of molecules A and B with masses m_A and m_B, k_B is the Boltzmann constant, E_a is the activation energy and p is a steric factor.

EXAMPLE 20.14 The rate constant at 27°C for a reaction is $1.3 \times 10^{-3}\ \text{s}^{-1}$ and its frequency factor is $2.785 \times 10^6\ \text{s}^{-1}$. Determine its entropy and enthalpy of activation.

Solution

$$A = \frac{k_bT}{h}\, e^{\Delta S^*/R}$$

or
$$\log A = \log \frac{k_bT}{h} + \frac{\Delta S^\circ}{2.303\, R}$$

$$A = 2.785 \times 10^6\ \text{s}^{-1},\ k = 1.3 \times 10^{-3}\ \text{s}^{-1},\ T = 273 + 27 = 300\ \text{K}$$

$$h = 6.62 \times 10^{-27}\ \text{erg s},\quad R = 1.98\ \text{cal K}^{-1}\ \text{mol}^{-1}$$

$$\log 2.785 \times 10^6 = \log \frac{1.38 \times 10^{-3} \times 300}{6.62 \times 10^{-27}} + \frac{\Delta S^\circ}{1.98 \times 2.303}$$

$$6.4448 = 12.7963 + \frac{\Delta S^*}{1.98 \times 2.303}$$

$$\Delta S^* = -29.06\ \text{e.u.}$$

$$\text{Now, } k = \frac{k_bT}{h}\, e^{\Delta S^*/R} \times e^{-\Delta H^*/RT}$$

$$= A\, e^{-\Delta H^*/RT}$$

$$\log k = \log A - \frac{\Delta H^*}{2.303\, RT}$$

$$\log 1.3 \times 10^{-3} = \log 2.785 \times 10^6 - \frac{\Delta H^*}{2.303 \times 1.98 \times 300}$$

$$\frac{\Delta H^*}{2.303 \times 1.98 \times 300} = 6.4448 - \bar{3}.1139$$

$$= 9.3309$$

$$\Delta H^* = 12.8 \text{ kcal mol}^{-1}$$

20.12 STEADY STATE HYPOTHESIS

According to the steady state hypothesis, the rate of change of concentration of the reactive intermediates is assumed to be zero, i.e. $\frac{d\,[C_i]}{dt} = 0$, where C_i is the concentration of the reactive intermediate. For example, the rate of decomposition of acetaldehyde can be obtained by using steady state hypothesis

$$CH_3CHO \xrightarrow{k_1} \dot{C}H_3 + \dot{C}HO$$

$$\dot{C}H_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3\dot{C}O$$

$$CH_3\dot{C}O \xrightarrow{k_3} \dot{C}H_3 + CO$$

$$\dot{C}H_3 + \dot{C}H_3 \xrightarrow{k_4} C_2H_6$$

According to the steady state hypothesis,

$$\frac{d\,[\dot{C}H_3]}{dt} = 0 = k_1[CH_3CHO] - k_2[\dot{C}H_3]\,[CH_3CHO] + k_3[CH_3\dot{C}O]$$

$$-k_4[\dot{C}H_3]^2 \qquad \text{(i)}$$

and $$\frac{d\,[CH_3\dot{C}O]}{dt} = 0 = k_2[\dot{C}H_3]\,[CH_3CHO] + k_3[CH_3\dot{C}O] \qquad \text{(ii)}$$

From (i) and (ii),

$$k_4\,[\dot{C}H_3]^2 = k_1\,[CH_3CHO]$$

$$\therefore \qquad [\dot{C}H_3] = \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{1}{2}}$$

The rate of reaction is given by

$$\frac{-d\,[CH_3CHO]}{dt} = k_1\,[CH_3CHO] + k_2\,[CH_3]\,[CH_3CHO]$$

Since the chain initiation step is much slower than the chain propagation step.

$$\frac{-d\,[CH_3CHO]}{dt} \approx k_2\,[CH_3]\,[CH_3CHO] = k_2\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{3/2}$$

Rate of decomposition of acetaldehyde $= k\,[CH_3CHO]^{3/2}$

20.13 CATALYSIS

It has been observed that, in many cases, the rate of a reaction is considerably affected by the presence of some foreign substance in the reaction mixture. This added substance is called a *catalyst.*

A substance which can influence (enhance) the rate of a chemical reaction and is recovered at the end of the reaction without any change in its chemical composition is called a catalyst and the phenomenon is called *catalysis.*

Let us define some terms used in catalysis.

Auto Catalysis

In some reactions, the product formed is itself a catalyst and, therefore, the rate will become faster as the reaction proceeds. Such reactions are called *autocatalysed* and the phenomenon is known as autocatalysis. For example, oxidation of oxalic acid by the permanganate ion is catalysed by the Mn^{2+} ion, which is also a product of the reaction:

$$2MnO_4^- + 6H^+ + 5(COOH)_2 \rightleftharpoons 2Mn^{2+} + 10CO_2 + 8H_2O$$

Promoters

Some substances do not act as catalysts but enhance the efficiency of a catalyst. Such substances are known as *promoters.* For example, M_o acts as promoter in the synthesis of ammonia by the Haber process, in which iron is used as a catalyst.

Negative Catalysts or Inhibitors

A substance, which instead of increasing the rate of a reaction actually decreases it, is called an *inhibitor or negative catalyst.* These are also of industrial importance and are used in stabilizing otherwise unstable substances. For example, small amounts of acetanilide are added to commercial hydrogen peroxide for stabilization.

Catalytic Poisons

Impurities in the reactants sometimes adversely affect the efficiency of a catalyst. Such substances are called catalytic poisons. For example, in the Contact process in which SO_2 and O_2 combine over the catalyst to give SO_3, the catalyst is adversely effected by the presence of arsenic (called catalytic poison).

20.14 CHARACTERISTICS OF CATALYSED REACTIONS

(a) The amount and chemical composition of the catalyst remains unchanged.

Time min	C mol dm^{-3}	$\frac{k}{\text{min}^{-1}} = \frac{2.303}{t} \log \frac{C_0}{C}$	$\frac{k}{\text{mol}^{-1}\ \text{dm}^3\ \text{min}^{-1}} = \frac{1}{t} - \left[\frac{1}{C} - \frac{1}{C_0}\right]$
0	0.1000	—	—
10	0.0714	0.0343	0.400
20	0.0556	0.0342	0.399
40	0.0385	0.0239	0.399
100	0.0200	0.0161	0.400
125	0.0167	0.0062	0.399

It can be seen from column 3 that k is not constant. Hence the reaction is not of first order. Let us now try the second order rate equation,

$$k = \frac{1}{t}\left(\frac{1}{C_A} - \frac{1}{C_{A0}}\right)$$

It can be seen from column 4 that the second order k is nearly constant at different times. Therefore, the given reaction is second order with rate constant 0.400 mol^{-1} dm^3 min^{-1}.

Example 20.16 Show that, for the nth order reaction in A, the rate constant

$$k = \frac{1}{t\,(n-1)}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]^{n-1}$$

and half-life period

$$t_{\frac{1}{2}} = \frac{2^{n-1}-1}{(n-1)\,k_n\,[A_0]^{n-1}}$$

where [A] is the concentration of A at time t

Solution Consider the reaction

$$A \longrightarrow \text{Products}$$

For the nth order in A,

$$\text{Rate} = -\frac{d\,[A]}{dt} = k\,[A]^n$$

or

$$= -\frac{d\,[A]}{[A]^n} = k\,dt$$

On integrating,

$$\frac{1}{n-1}\,\frac{1}{[A]^{n-1}} = kt + \text{constant}$$

At $t=0$, constant $= \dfrac{1}{(n-1)}\,\dfrac{1}{[A_0]^{n-1}}$

or

$$kt = \frac{1}{n-1}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}}\right]$$

or

$$k = \frac{1}{t\,(n-1)}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]^{n-1}$$

The half-life period can be calculated as

At time $= t_{\frac{1}{2}}$, $[A] = [A_0]/_2$

$$k = \frac{1}{t_{\frac{1}{2}}\,(n-1)}\left[\frac{1}{[A]} - \frac{1}{[A_0]}\right]^{n-1}$$

or

$$t_{\frac{1}{2}} = \frac{1}{k\,(n-1)}\left[\left(\frac{2}{[A_0]}\right)^{n-1} - \left(\frac{1}{[A_0]}\right)^{n-1}\right]$$

$$= \frac{2^{n-1}-1}{(n-1)\,k[A_0]^{n-1}}$$

QUESTIONS

Numerical Problems

20.1 The reaction A ⟶ P has been found to be third order with respect to A

(a) Write the rate expression for the reaction.

(b) What are the units of its rate constant if the concentrations are expressed in mol dm^{-3} and time in min.

(c) Show that for this reaction

$$t_{\frac{1}{2}} = \frac{3}{2ka^2}$$

where a is the initial concentration of A and $t_{\frac{1}{2}}$ is the half-life time.

20.2 (SI units) In the reaction

$$2N_2O_5 \longrightarrow 2N_2O_4 + O_2$$

the concentration of N_2O_5 changes from 0.3 mol dm^{-3} to 0.024 mol dm^{-3}, in 30 min. Calculate

(a) the average rate of disappearance of N_2O_5

(b) the average rate of the reaction

(c) the average rate of production of oxygen

20.3 (SI units) The rate of a first order reaction is equal to 1.3×10^{-3} mol dm^{-3} s^{-1} when the concentration of the reactant is 0.26 mol dm^{-3}. Determine the first order rate constant in seconds, minutes and hours.

20.4 (SI units) What will be the initial rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol dm^{-3}? How much of it will be converted into products in 20 min ?

20.5 The acidic hydrolysis of ethyl acetate taking place according to the reaction.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

is first order in ethyl acetate, water and hydrogen ion. However, due to the large concentration of H_2O (≈ 55 mol dm^{-3}) and constant concentration of H^+ (acetic acid produced during the reaction remain undissociated) the reaction becomes first order in ester. When the hydrolysis was carried in 0.5 M HCl by titrating the reaction mixture against 0.1 N NaOH, the following results were obtained:

Time (min)	0	20	24	45	56	70	96	136	∞
Vol. of 0.1 N NaOH required	23.7	27.7	27.2	29.7	30.8	32.1	34.1	36.4	41.4

(a) Determine the pseudo first order rate constant

(b) What will be the true third order rate constant ?

20.6 The following data for the decomposition of azoisopropane at 270°C was obtained:

Time (s)	0	180	360	540	720	1020
Pressure (torr)	35.15	46.30	53.90	58.85	62.20	65.50

Find the order of this reaction and the rate constant.

20.7 The saponification of methylacetate by an alkali was found by the neutralisation of the alkali by an acid. Determine the order of the reaction if the initial concentrations of methylacetate and sodium hydroxide are both equal to 0.01 M and the concentration of sodium hydroxide at different intervals was

Time (min)	3	5	10	15
Concentration (NaOH) (mol dm^{-3})	0.00743	0.00635	0.00464	0.02363

20.8 In 50 min, a first order reaction goes to 40% completion. Calculate its half life period and the rate constant for the reaction.

20.9 The reaction $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$
is a first order reaction with rate constant $= 2.2 \times 10^{-5}$ s^{-1} at 575 K. In how much time will it be decomposed to 20%, when the reaction is carried out at 575 K ?

20.10 The half life period of a substance is 80 min at a certain concentration. When the concentration is reduced to one half the inital concentration, the half life period is 40 min. Calculate the order of the reaction.

20.11 The half life period for a second order reaction with initial concentration 0.425 mol dm^{-3} is 500 s. Calculate the rate constant.

20.12 For the reaction

$$A \longrightarrow \text{Products}$$

the following data were obtained at 25°C, in which the concentration of A is given at different intervals of time:

t (min)	0	10	20	30	50
[A] mol dm^{-3}	0.860	0.740	0.635	0.546	0.405

Calculate the order of the reaction and the half-life period.

20.13 At a certain temperature, the half life periods and initial concentrations for a reaction are

$$t_{\frac{1}{2}} = 420 \text{ s}, \ a = 0.405 \text{ mol dm}^{-3}$$

$$t_{\frac{1}{2}} = 275 \text{ s}, \ a = 0.64 \text{ mol dm}^{-3}$$

Calculate the order of the reaction and the rate constant.

20.14 The rate constants for a reaction at 30° and 40°C are 1.2×10^{-3} and 2.1×10^{-3} s^{-1}, respectively. What is its activation energy ?

20.15 The activation energy for a reaction is 22.5 kcal, whereas the value for its rate constant at 40°C is 1.8×10^{-5} s^{-1}. What is its frequency factor ?

20.16 Calculate the activation energy for the saponification of ethyl acetate by sodium hydroxide, if the temperature coefficient k_{35}/k_{25} is 1.8.

20.17 The rate constant for a reaction at 25°C is 3.46×10^{-5} s^{-1} and its activation energy is 103.9 kJ mol^{-1}. Calculate its rate constant at 35°C.

20.18 For a first order reaction, activation energy is 104.5 kJ mol^{-1} and the pre-exponential factor A in the Arrhenius equation is 5×10^{13} s^{-1}. At what temperature will the reaction have a half life of 1 minute ?

20.19 The rate constant for the forward reaction is 1.2×10^{-3} min^{-1} at 30°C. The enthalpies of activation and reaction are 20.4 kcal mol^{-1} and -25.6 kcal mol^{-1}, respectively. The rate constant for the reverse reaction is 1.2×10^{-4} at 50°C. What is its value at 40°C ?

20.20 Show that, for the third order reaction of the type

$$3A \longrightarrow \text{Products}$$

Rate constant, $k = \frac{1}{2t}\left[\frac{1}{C_A{}^2} - \frac{1}{C_{A_0}{}^2}\right]$

and half-life period, $t_{\frac{1}{2}} = \frac{3}{2k\,(C_{A_0})^2}$

QUIZ QUESTIONS

Type A: Multiple Choice

20.21 For the single-step reaction

$$2A + B \longrightarrow A_2B$$

the rate law is

(a) Rate $= k\,[A]\,[B]$
(b) Rate $= k\,[2A]\,[B]$
(c) Rate $= k\,[A]^2\,[B]$
(d) Rate $= \frac{k\,[A]^2\,[B]}{[A_2B]}$

20.22 If the units of concentration are mol dm^{-3} and of time are s, the units of the rate constant for a second order reaction will be

(a) dm^3 mol s^{-1}
(b) mol dm^{-3} s^{-1}
(c) dm^3 mol^{-1} s^{-1}
(d) dm^{-3} mol^{-1} s^{-1}

20.23 For the reaction

$$P + 2Q \longrightarrow R$$

the rate law is: rate $= k\,[P]\,[Q]$

If the reaction proceeds in two steps the rate determining step is

(a) $P + Q \longrightarrow R$
(b) $P + Q \longrightarrow$ intermediate
(c) $Q + Q \longrightarrow$ intermediate
(d) $P + 2Q \longrightarrow R$

20.24 The rate expression for a chemical reaction

$$2NO_2F \longrightarrow 2NO_2 + F_2$$

is given as: Rate $= k\,[NO_2F]$

The rate determining step might be

(a) $2NO_2F \longrightarrow 2NO_2 + F_2$
(b) $NO_2F + F \longrightarrow NO_2 + F_2$
(c) $NO_2F \longrightarrow NO_2 + F$
(d) $NO_2 + F \longrightarrow NO_2F$

20.25 For a reaction of the type

$$A + B \longrightarrow \text{Products}$$

it is observed that doubling the concentration of A causes the reaction rate to be four times as great, but doubling the amount of B there is no apparent effect on the rate. The rate equation is

(a) Rate $= k\,[A]\,[B]$
(b) Rate $= k\,[A]^2$
(c) Rate $= k\,[A[^2\,[B]$
(d) Rate $= k\,[A]^2\,[B]^2$

20.26 Consider the first order reaction.

$$A \longrightarrow B$$

If the initial concentration of A is a and B zero, and at any time t the concentration of B is x, then the rate equation can be written as

(a) $k = -\frac{1}{t} \ln \frac{(a-x)}{a}$

(b) $kt = \ln (a-x)$

(c) $kt = \ln \frac{a}{(a-x)}$

(d) $\frac{k}{t} = \ln \frac{a}{(a-x)}$

20.27 If C_A is the concentration of A at any time and C_A° is its concentration at $t = 0$, then, for a zero-order reaction of the type A ⟶ Products, the rate equation can be written as

(a) $C_A - C_A^0 = 0$

(b) $C_A = C_A^0 - k$

(c) $C_A/C_A^0 = k$

(d) $C_A = C_A^0 - kt$

20,28 For a reaction of the type (second order in A)

$$A \longrightarrow \text{Product}$$

if the initial concentration of A is a and at a given time t, the concentration of product is x, the rate constant (k) can be put as

(a) $k = t\,(a-x)$

(b) $k = t\left(\frac{1}{(a-x)} - \frac{1}{a}\right)$

(c) $k = \frac{1}{t}\left(\frac{1}{(a-x)} - \frac{1}{a}\right)$

(d) $k = \frac{1}{t}\left(\frac{a-x}{a}\right)$

20.29 If R_1 and R_2 are the rates of reactions at concentrations C_1 and C_2 of a reactant, then the order of the reaction (n) with respect to the reactant under consideration (keeping other factors such as concentrations of other reactants and temperature constant) is

(a) $n = \log \frac{R_1 C_1}{R_2 C_2}$

(b) $n = \frac{\log R_1 - \log R_2}{\log C_1 - \log C_2}$

(c) $n = \log \frac{C_2 - C_1}{R_2 - R_1}$

(d) $n = \frac{\log C_1 - \log C_2}{\log R_1 - \log R_2}$

20.30 The half-life period of any first order reaction

(a) is half the specific rate constant

(b) is independent of the initial concentration

(c) is always the same whatever the reaction

(d) is directly proportional to the initial concentration of the reactant

20.31 Consider the third order rate equation:

$$k = \frac{1}{2t}\left(\frac{1}{C^2} - \frac{1}{C^2}\right)$$

where C_0 is the initial concentration and C is the concentration at time t. The half life period ($t_{\frac{1}{2}}$) is

(a) $t_{\frac{1}{2}} = \frac{1}{k\,C_0}$ (b) $t_{\frac{1}{2}} = \frac{3k}{2C_0^2}$

(c) $t_{\frac{1}{2}} = \frac{3}{2k\,C_0^2}$ (d) $t_{\frac{1}{2}} = \frac{3}{2k\,C_0}$

20.32 Suppose that the rate law for reaction is

$$\text{Rate} = k\,[A]\,[B]$$

and the initial concentrations of A and B are equal. If C represents the concentration of both A and B at any time t, a straight line will be obtained if

(a) $1/C$ is plotted against t
(b) $1/C^2$ is plotted against t
(c) $\log C$ is plotted against t
(d) $\log C^2$ is plotted against t

20.33 For a reaction

$$A + B \longrightarrow C$$

the following kinetic data are obtained

Observation	A	B	Rate
1	0.1	0.2	0.01
2	0.2	0.2	0.04
3	0.2	0.8	0.08

The overall order of the reaction is

(a) 3 (b) 2
(c) 1.5 (d) 2.5

20.34 A catalyst increases the rate of a reaction because

(a) it provides the necessary energy to the colliding molecules to cross the energy barrier
(b) It decreases the heat of the reaction
(c) It decreases the order of the reaction
(d) It provides a different path of lower activation energy

20.35 Chemical reactions of the type

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

are called

(a) pseudo chemical reactions
(b) consecutive reactions
(c) parallel reactions
(d) fast reactions

20.36 Consider a system containing NO_2 and SO_2, in which NO_2 is consumed in the following parallel reactions

$$2NO_2 \overset{k_1}{\rightleftharpoons} N_2O_4$$

$$NO_2 + SO_2 \overset{k_2}{\rightleftharpoons} NO + SO_3$$

the rate of disappearance of NO_2 will be equal to

(a) $k_1\,[NO_2]^2 + k_2\,[NO_2]\,[SO_2]$
(b) $2k_1\,[NO_2]^2$
(c) $2k_1\,[NO_2]^2 + k_2\,[NO_2]\,[SO_2]$
(d) $k_1\,[NO_2]^2 + k_2\,[NO_2]$

20.37 In a reversible reaction

$$2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$$

the rate of disappearance of NO_2 is equal to

(a) $2k_1\,[NO_2] - k_2\,[N_2O_4]$

(b) $2k_1 [NO_2]^2 - k_2 [N_2O_4]$
(c) $(2k_1 - k_2) [NO_2]$
(d) $2k_1/k_2 [NO_2]$

20.38 For the first-order reaction with rate constant k, the half-life period (initial concentration $= a$) is equal to

(a) $\frac{\ln 2}{k}$ (b) $\frac{1}{ka}$

(c) $\frac{0.693}{ka}$ (d) $\frac{1}{ka_{\frac{1}{2}}}$

20,39 The equation for the rate constant is given by

$$k = p\ Ze^{-E_a/RT}$$

a chemical reaction will proceed more rapidly if there is a decrease in

(a) T (b) Z

(c) E_a (d) p

20.40 The large increase in the rate of a reaction on rise in temperature is due to

(a) the lowering of activation energy
(b) the decrease in mean free path
(c) the increase in collision frequency
(d) the increase in the number of molecules having more than the threshold energy

20.41 In the kinetic study of a reaction

$$A \longrightarrow \text{Products}$$

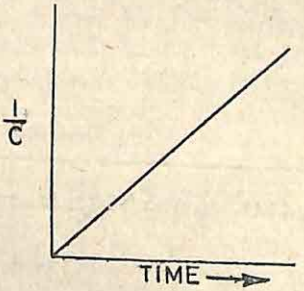
a straight line was observed when a graph between time and $1/C^2$ was plotted, The reaction is

(a) second order (b) third order

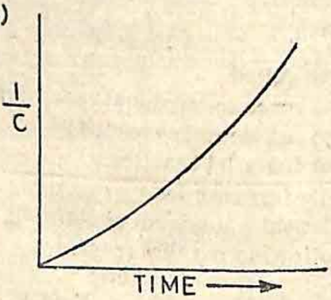
(c) zero order (d) first order

20.42 Which of the following graphs corresponds to a second-order reaction:

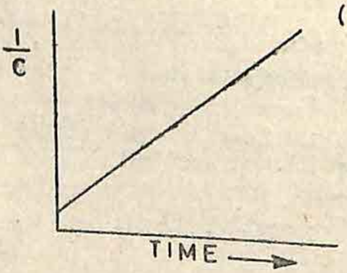
(a)



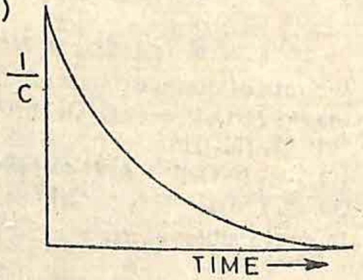
(b)



(c)



(d)



20.43 For an nth order reaction, the half-life period $t_{\frac{1}{2}}$ is proportional to [if initial concentration $= (C_0)$]

(a) $\frac{1}{C_0^n}$ (b) C_0^{n-1}

(c) $\frac{1}{C_0^{n-1}}$ (d) $\frac{0.693}{C_0^n}$

20.44 Which of the followings is not an example of homogeneous catalysis

(a) $CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3OH + CH_3COOH$

(b) $SO_2 + \frac{1}{2}O_2 \xrightarrow{Pt} SO_3$

(c) $SO_2 + \frac{1}{2}O_2 \xrightarrow{NO} SO_3$

(d) $CH_3COOC_2H_5 + H_2O \xrightarrow{OH^-} CH_3COOH + C_2H_5OH$

20.45 Which of the followings is not a true characteristic of a catalytic reaction,

(a) The amount and chemical composition of the catalyst remains unchanged after the reaction.

(b) The catalyst does not initiate a chemical reaction.

(c) The reaction in which products also act as catalysis are called autocatalysed reactions.

(d) The catalyst shifts the equilibrium position of a reaction in a favourable direction.

Type B: Multiple Choice (Numerical Problems)

20.46 The rate of a first order reaction is 1.5×10^{-3} mol l^{-1} min^{-1} when the concentration of the reactant is 0.5 mol l^{-1}. The rate constant in seconds is

(a) 3×10^{-3}

(b) 0.18

(c) 5×10^{-5}

(d) 7.5×10^{-4}

20.47 The half-life time for a reaction at initial concentrations 0.1 and 0.4 mol l^{-1} are 3′ 20″ and 50″, respectively. The order of the reaction is

(a) 1 (b) 2 (c) 3 (d) 4

20.48 A first-order reaction has a half-life period of 69.3 seconds. Its rate constant is

(a) 10^{-2} s^{-1}

(b) 10^{-4} s^{-1}

(c) 10 s^{-1}

(d) 10^{2} s^{-1}

20.49 The rate of a second order reaction is 3×10^{-5} mol l^{-1} s^{-1}. When the initial concentration is 0.2 mol l^{-1}, the rate constant k is

(a) 1.5×10^{-4}

(b) 7.5×10^{-4}

(c) 7.5×10^{-3}

(d) 1.5×10^{-3}

20.50 The following data are given for a reaction:

Conc. A.	1	1	0.02	0.04 (mol l^{-1})
Conc. B.	0.02	0.04	1	1
Rate (mol l^{-1} min^{-1})	1.5×10^{-3}	3×10^{-3}	3×10^{-3}	1.2×10^{-2}

The order of the reaction is

(a) 1 (b) 1.5 (c) 2 (d) 3

20.51 The rate for a first order reaction is 1.8×10^{-3} mol dm^{-3}min^{-1} when the initial concentration is 0.3 mol dm^{-3}. The rate constant in the units of seconds is

(a) 1×10^{-2} s^{-1}

(b) 1×10^{-4} s^{-1}

(c) 6×10^{-3} s^{-1}

(d) 6×10^{-2} s^{-1}

20.52 The rate for a first order reaction is 0.69×10^{-2} mol l^{-1} min^{-1} and the initial concentration is 0.2 mol dm^{-3}. The half-life period is
(a) 1200 s (b) 0.33 s (c) 1 s (d) 600 s

20.53 The half-life time for a reaction at initial concentrations 0.5 and 1.0 mol dm^{-3} are 3 min 20 s and 1 min 40 s, respectively. The order of the reaction is
(a) zero (b) one (c) two (d) three

20.54 The rate constant for a zero-order reaction is 4×10^{-2} mol dm^{-3} s^{-1}. The concentration of the reactant after 25 s is 0.5 mol dm^{-3}. The initial concentration was
(a) 1.25 mol dm^{-3}
(b) 0.125 mol dm^{-3}
(c) 1.5 mol dm^{-3}
(d) 0.5 mol dm^{-3}

20.55 For a third order reaction, the rate constant is 2.5×10^{-2} mol^{-2} dm^{6} s^{-1}. If the initial concentration is 0.1 mol dm^{-3}, the half life period will be
(a) 100 min (b) 600 min (c) 60 min (d) 6 min

Type C: True or False

20.56 If the activation energy of a reaction is low, the reaction is relatively faster.

20.57 For an exothermic reaction, the activation energy for the forward reaction is always less than the activation energy for the backward reaction.

20.58 In a multistep reaction, the fastest step determines the overall rate of the reaction.

20.59 Many body collisions have low probabilities.

20.60 The activation energy is the difference in energy content between the transition state and the ground state of the reactants.

20.61 According to Arrhenius' equation, the rate constant increases exponentially with temperature and should become equal to A when T is zero.

20.62 In a third order reaction, $t_{\frac{1}{2}}$ is inversely proportional to the square of the initial concentration.

20.63 A reaction of the type $A \rightarrow B \rightarrow C$ is called a parallel reaction.

20.64 The increase in reaction rates with temperature is due to the increase in collision frequency.

20.65 For a single-step reaction, the law of mass action and the rate law expressions are same.

20.66 In a reversible reaction, the rate of the forward reaction is always equal to that of the backward reaction.

20.67 Molecularity has significance only for elementary reaction.

20.68 According to the steady state hypothesis, the rate of change of concentration of the reactive intermediates is assumed to be very high.

20.69 Substances which do not act as catalysts but enhance the efficiency of a catalyst are called autocatalysts.

20.70 The catalysed reaction generally has a lower activation energy than the uncatalysed reaction.

Type D: Fill in the Blanks

20.71 In a multistep reaction, the order of the reaction is determined from the ———— step.

20.72 The minimum amount of energy which the colliding molecules must have in order to bring about a reaction is known as————.

20.73 Reactions which occur under the influence of radiant energy are called ———— reactions.

20.74 The stepwise description of a chemical reaction is called————of the reaction.

20.75 The order of a reaction with respect to reactant A, whose rate law is, rate $=k[A][B]^2[C]^{\frac{1}{2}}$ is————.

20.76 A catalyst does not shift the position of ————of a reaction.

20.77 The difference between the energy maximum along a reaction path and the energy of the reactant is called————.

20.78 The sum of powers to which the concentration terms are raised in the rate law is called————of the reaction.

20.79 A substance which decreases the rate of a reaction is called————.

20.80 For a first order reaction, the half-life period is equal to————.

ANSWERS

Numerical Problems

20.1 (a) Rate $= k[A]^3$ (b) $\text{mol}^{-2}\ \text{dm}^6\ \text{min}^{-1}$ *20.2* – 0.0002 (b) 0.0001 (c) 0.0001 *20.3* $5 \times 10^{-3}\ \text{min}^{-1}$, $0.3\ \text{h}^{-1}$, $8.3 \times 10^{-5}\ \text{s}^{-1}$ *20.4* $0.2 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{min}^{-1}$, $0.196\ \text{mol dm}^{-3}$ *20.5* 0.00921, 3.34×10^{-4} *20.6* First order, 0.00206 *20.7* Second order, 11.69 *20.8* 67.8 min, $0.01022\ \text{min}^{-1}$ *20.9* 169 min *20.10* zero order *20.11* 4.7×10^{-3} *20.12* 0.0151, 45.9 min *20.13* 2, 5.88×10^{-3} *20.14* 10.5 kcal *20.15* $9.3 \times 10^{10}\ \text{s}^{-1}$ *20.16* 10.7 kcal *20.17* $13.5 \times 10^{-5}\ \text{s}^{-1}$ *20.18* 75°C *20.19* 1.21×10^{-5}

Quiz Questions

20.21 (c) *20.22* (c) *20.23* (b) *20.24* (c) *20.25* (b) *20.26* (c) *20.27* (b) *20.28* (c) *20.29* (b) *20.30* (b) *20.31* (c) *20.32* (a) *20.33* (d) *20.34* (d) *20.35* (b) *20.36* (c) *20.37* (b) *20.38* (a) *20.39* (c) *20.40* (d) *20.41* (b) *20.42* (c) *20.43* (c) *20.44* (b) *20.45* (d) *20.46* (c) *20.47* (b) *20.48* (a) *20.49* (b) *20.50* (d) *20.51* (b) *20.52* (a) *20.53* (c) *20.54* (c) *20.55* (a) *20.56* True *20.57* True *20.58* False *20.59* True *20.60* True *20.61* False: Arrhenius' equation is $k = a\,e^{-E_0/RT}$ and k becomes equal to A when T is infinity *20.62* True *20.63* False: It is called consecutive reaction *20.64* False *20.65* True *20.66* False: The rates of forward and backward reactions are equal only at equilibrium *20.67* True *20.68* False *20.69* False *20.70* True *20.71* slowest *20.72* threshold *20.73* photochemical *20.74* mechanism *20.75* 1 *20.76* equllibrium *20.77* activation energy *20.78* Order *20.79* inhibitor *20.80* $\dfrac{0.693}{k}$.

Lambert–Beer's Law

Lambert's law states that when a beam of monochromatic light passes through a homogeneous absorbing medium, the light absorbed by each infinitesimally small layer is proportional to the intensity of the light entering it and the thickness of the layer.

When light of intensity I is absorbed in a layer of thickness between x and $x+dx$, and dI is the light absorbed, then, according to the above law,

$$-dI = a\,I\,dx \tag{21.5}$$

where a is the absorption coefficient. On integrating Eq. (21.5), we get

$$I = I_0\, e^{-ax} \tag{21.6}$$

where I_0 is the intensity of the incident beam and I is the intensity after absorption. Therefore, the difference between I_0 and I gives the intensity of the light absorbed, i.e.

$$\begin{aligned} I_{\text{abs}} &= I_0 - I = I_0 - I_0\, e^{-ax} \\ &= I_0\,(1-e^{-ax}) \end{aligned} \tag{21.7}$$

Beer's law is an extension of Lambert's law, put forward by Beer (1852). According to this law, the absorption coefficient of the medium is also proportional to the concentration of the solution and can be expressed as

$$a = \varepsilon' c$$

where ϵ' is called the *molar absorption coefficient* and c is the molar concentration of the solute. Therefore, the Lambert law for solutions and gases may be written as

$$I = I_0\, e^{-\epsilon' cx} \tag{21.8}$$

$$\text{or} \quad I = I_0\, 10^{-\epsilon' cx/2.303} = I_0\, 10^{-\epsilon cx} \tag{21.9}$$

where ε ($\epsilon'/2.303$) is known as the *molar extinction coefficient*. The relation (21.9) is called the Beer-Lambert law or simply Beer's law.

The quantity ϵcx is called the *optical density* (O.D.) of a solution and is equal to $\log (I_0/I)$.

Stark-Einstein's law was put forward by Stark (1908) and Einstein (1912). According to this law, each molecule taking part in a photochemical reaction takes up one quantum of the radiation causing the reaction.

In other words, a molecule, before reacting photochemically, must absorb one quantum ($h\nu$) of energy. This is also known as the *law of photochemical equivalence*. More vigorously, this may be stated as:

In a primary process* one photon is required for the excitation of a molecule. An excited (activated) molecule can undergo a number of photophysical and/or chemical processes.

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*Refer section 21.6.

This principle does not mean that one molecule reacts with the absorption of each photon because, due to the secondary thermal reaction involving free radicals, a large number of molecules may react per photon. Alternatively, molecules may be deactivated by other processes and only a fraction may react per absorbed photon.

EXAMPLE 21.3 The extinction coefficient of $K_3[Fe(CN)_6]$ at 419 nm is 1020 $cm^2\ mol^{-1}$. What percentage of light is transmitted from a cell of thickness 2 cm containing $\frac{M}{10,000}$ $K_3[Fe(CN)_6]$ solution ?

Solution Light transmitted by the medium,

$$I = I_0\, 10^{-\epsilon c x}$$

Fraction of light transmitted

$$\frac{I}{I_0} = 10^{-\epsilon c x}$$

$$\epsilon = 1020 \text{ cm}^2 \text{ mol}^{-1}, \qquad x = 2 \text{ cm},$$

$$c = \frac{M}{10,000} = \frac{1}{10,000} \text{ mol dm}^{-3}$$

$$\frac{I}{I_0} = 10^{-1020\times\frac{1}{10,000}\times 2} = 10^{-0.204}$$

$$\text{Percentage of light transmitted} = \frac{I}{I_0}\times 100 = 100\times 10^{-0.204}$$

$$= 62.5\%$$

EXAMPLE 21.4 The optical density of a 0.001 M solution of A in a cell of 0.1 cm path length is 0.162. What is the extinction coefficient of A ?

Solution

$$\text{Optical density, O.D.} = \epsilon\, c\, x$$

$$\text{O.D.} = 0.162, \qquad c = 0.001 \text{ M}, \qquad x = 0.1$$

$$\therefore \quad \epsilon = \frac{\text{O.D.}}{cx}$$

$$= \frac{0.162}{0.001\times 0.1} = 1.62\times 10^3 \text{ cm}^2 \text{ mol}^{-1}$$

EXAMPLE 21.5 A light beam of flux 10^{19} photons $cm^{-2}\ s^{-1}$ passes through a 10 cm long cell containing a 0.5×10^{-4} M solution of a substance with an extinction coefficient of 1050 $cm^2\ mol^{-1}$. How much energy is absorbed per second by the solution if the wavelength of the light is 470 nm ? The cross-section of the cell through which the light passes is 1 cm^2.

Solution The intensity of light transmitted

$$I = I_0\, 10^{-\epsilon c x}$$

$$I_0 = 10^{19} \text{ photons cm}^{-2} \text{ s}^{-1}, \ \epsilon = 1050 \text{ cm}^2 \text{ mol}^{-1},$$

$$c = 0.5\times 10^{-4} \text{ M}$$

$$x = 10 \text{ cm}$$

$$\text{Number of photons transmitted} = I = 10^{19} \times 10^{-(1050)\,(0.5\times10^{-4})\times10}$$
$$= 10^{19} \times 10^{-0.525}$$
$$= 2.985 \times 10^{18} \text{ photons cm}^{-2}\text{ s}^{-1}$$

Since the cross-section of the cell is 1 cm^2, the number of photons transmitted per second = 2.985×10^{18} photons s^{-1}

$$\text{Number of photons absorbed per second} = I_0 - I$$
$$= 10^{19} - 2.985 \times 10^{18}$$
$$= 7.015 \times 10^{18} \text{ photons s}^{-1}$$

$$\text{Wavelength of light } \lambda = 470 \text{ nm} = 470 \times 10^{-9} \text{ m}$$

$$\text{Frequency of light, } \nu = \frac{c}{\lambda} = \frac{3 \times 10^{8} \text{ m s}^{-1}}{470 \times 10^{-9} \text{ m}}$$
$$= 6.383 \times 10^{14} \text{ s}^{-1}$$

$$\text{Energy of photon} = h\nu$$
$$\text{Energy of photons} = (6.62 \times 10^{-34} \text{ J s}) \times (6.383 \times 10^{14} \text{ s}^{-1})$$
$$= 42.255 \times 10^{-20} \text{ J}$$

$$\text{Energy of } 7.015 \times 10^{18} \text{ photons} = 42.255 \times 10^{-20} \times 7.015 \times 10^{18}$$
$$= 2.96 \text{ J}$$

Energy absorbed by the solution per second = Energy of 7.015×10^{18} photons of wavelength 470 nm = 2.96 J

21.3 CONCEPT OF EXCITED STATES

Electrons in the various molecular orbitals of a molecule in the ground state are distributed according to Pauli's exclusion principle and Hund's rule. Most molecules have an even number of electrons and, in the ground state, each orbital accommodates two electrons with opposite spin. The multiplicity of an electronic state is equal to $(2S+1)$ where S is the total spin (algebric sum of spin quantum numbers) for the molecule in the given electronic state. For $S = 0$, $\frac{1}{2}$ and 1, the multiplicity is 1, 2 and 3, respectively. When the electrons are either paired or have opposite spins, the net spin is zero, i.e. $S = 0$ so that $2S+1=1$. This state is called the *singlet state*. If the two electrons have the same spin, the total spin $S = \frac{1}{2}+\frac{1}{2} = 1$ so that the multiplicity is $2S+1 = 3$. This state is called the *triplet state* because, corresponding to this spin, there can be three states, i.e. its multiplicity is three. Most molecules* in their ground state are singlet. However, when an electron is excited to a higher orbital it may go with the same spin (total $S = 0$) or its spin quantum number

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*There are a number of exceptions, for example, the oxygen molecule is a triplet in the ground state, odd-electron molecules like NO are doublet in the ground state.

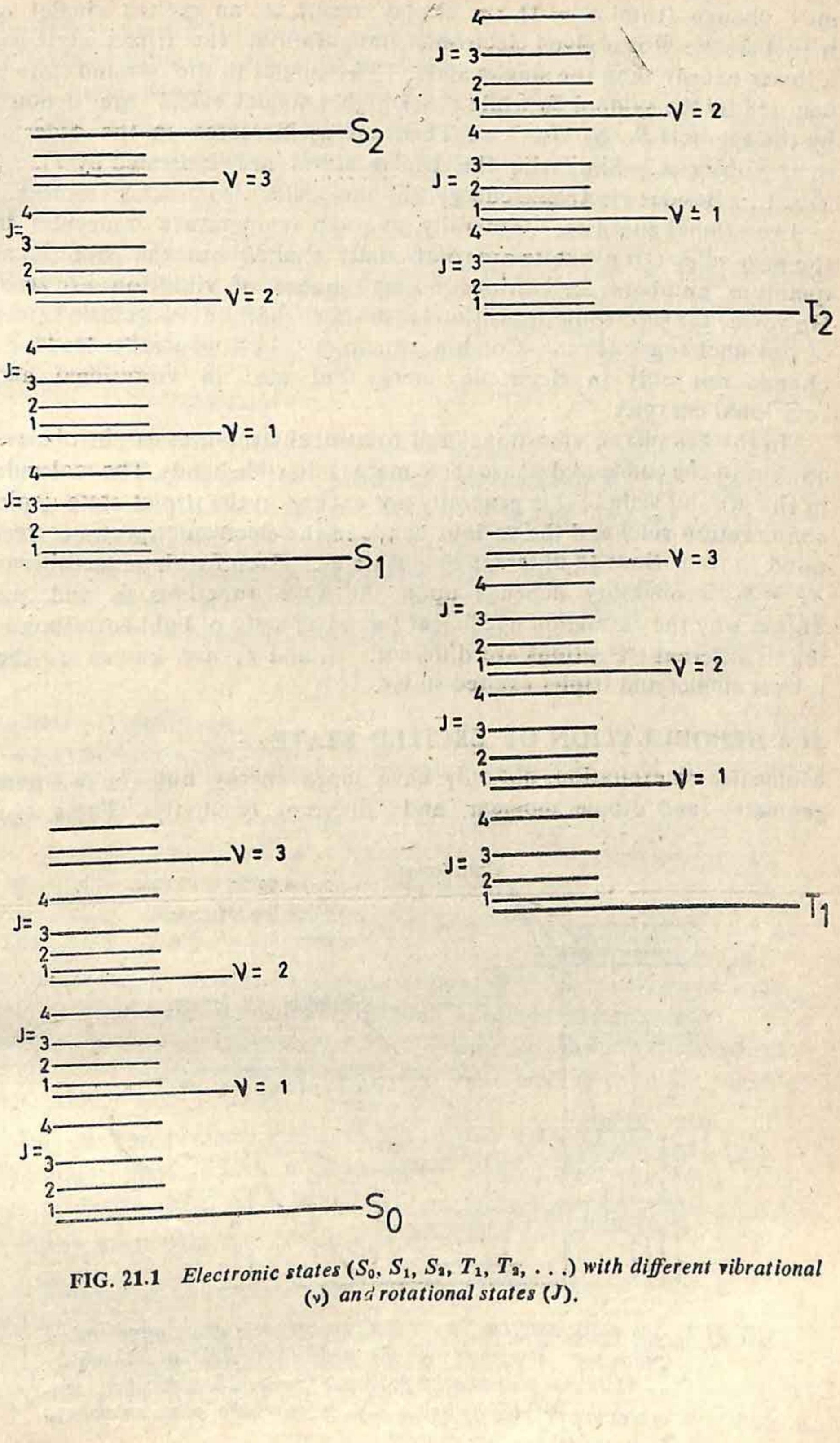


FIG. 21.1 *Electronic states (S_0, S_1, S_2, T_1, T_2, . . .) with different vibrational (v) and rotational states (J).*

may change (total $S = 1$), i.e. it may result in an excited singlet or triplet state. For a given electronic configuration, the triplet state has a lower energy than the singlet state. The singlet in the ground state is denoted by the symbol S_0 while other higher singlet states are denoted by the symbols S_1, S_2, S_3, ... Their energy increases in the order of their subscript. Similarly, the triplet states are indicated by T_1, T_2, T_3, ... Besides electronic energy, the molecules also possess vibrational and rotational energies. Generally, at room temperature molecules in the ground electronic state are rotationally excited but the vibrational quantum numbers for various normal modes of vibration are zero. However, the electronic transition is so fast that nuclei remain more or less unchanged (Frank-Condon principle). This generally leads to change not only in electronic energy but also in vibrational and rotational energies.

In the gas phase, vibrational and rotational structures can be observed, but in the condensed phase these merge into wide bands. The molecule in the ground state (S_0) is generally not excited to the triplet state (spin conservation rule) and the various bands in the electronic spectra correspond to transitions to different singlet states. Even for these transitions $S_n \leftarrow S_0$, probability depends upon the wave functions ψ_0 and ψ_n. This is why the extinction coefficient for wavelength of light corresponding to different transitions are different. S_1 and T_1 are known as the lowest singlet and triplet excited states.

21.4 DEPOPULATION OF EXCITED STATE

Molecules on excitation, not only have more energy but have new geometry and dipole moment, and different reactivity. These can

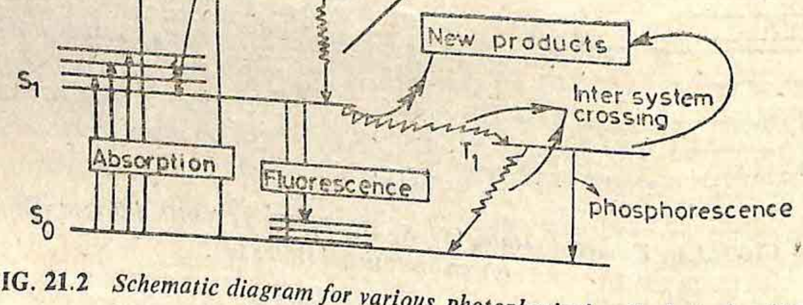


FIG. 21.2 *Schematic diagram for various photophysical and photochemical processes. Processes with the emission of light are shown by → while the non-radiative processes ⇝. Photochemical processes are denoted by and ⇾ ⇾ and may take place unimolecularly or with another molecule*

undergo a variety of processes. As a matter of fact, an excited molecule behaves as a different chemical species.

Processes which can bring the molecule intact to the ground state are called *photophysical processes*, while those leading to new products are called *photochemical processes*. Various photophysical and photochemical processes are shown in Fig. 21.2, known as the Jabolonski diagram.

The excited molecules may lose the energy and come to their ground state, either without emitting rediation (called non-radiative transitions) or by emitting radiation (called radiative transitions). In case of non-radiative transitions the energy is lost as heat.

Non-radiative Transitions

When the transition occurs between states of the same multiplicity without emitting light, it is called *internal conversion*. On the other hand, if the transition takes place between states of different multiplicity without emitting light, it is called *intersystem crossing*.

Internal conversion may take place both from a singlet or triplet state. However, the triplet state generally has longer life than the singlet state and, hence, is available for a larger time for a chemical reaction.

Radiative Transitions

These transitions give rise to two phenomena: *fluorescence* and *phosphorescence*.

Fluorescence It is the emission of light when the molecule returns to the ground state from an excited state of the same multiplicity. Fluorescence corresponds to transition $S_n \rightarrow S_0$. As most molecules in their ground state are singlet, fluorescence generally corresponds to the transition $S_1 \rightarrow S_0$.

Phosphorescence It is the emission of light when the molecule returns to the ground state from an excited state of a different multiplicity. For most molecules, phosphorescene corresponds to $T_1 \rightarrow S_0$. The wavelength of phosphorescent light is longer than that for fluorescence or absorption.

The excited molecule may undergo several other processes, such as quenching, photosensitization, excimer or exciplex formation. These may undergo chemical transformations by a unimolecular or bimolecular process.

21.5 CHEMILUMINESCENCE AND BIOLUMINESCENCE

Chemiluminescence is the emission of light in certain chemical reactions. Some reactions are highly exoergic so that some product molecules are obtained in the excited state. For example, in the reaction of sodium vapour with alkyl halides, we get an emission from the alkali metal atoms. The glow of yellow phosphorous is also due to chemiluminescence as a result of slow oxidation in air.

The emission of light in a biological reaction is called bioluminescence. In other words, bioluminescence is the chemiluminescence in a biological reaction. For example, the glow of the firefly is due to the oxidation of luciferin.

21.6 PRIMARY AND SECONDARY PROCESSES

It is sometimes desirable to distinguish between primary and secondary process.

A *primary process* is defined as a continuous sequence of steps which starts with the absorption of light. It is generally named after the last primary step. For example,

$$S_0 \xrightarrow{h\nu} S_2 \dashrightarrow S_1 \dashrightarrow S_1 \xrightarrow{-h\nu} S_1{}^0$$

The primary process is called fluorescence although it consists of the excitation of a molecule to the S_2 state which, by internal conversion, goes into S_1. This then relaxes vibrationally and gives S_1, emits light and goes to the ground state.

In secondary processes, certain intermediates are formed which react themselves to form the products. For example, in the photochemical combination of H_2 and Cl_2, the primary process is the dissociation of Cl_2 molecules into atoms as a result of absorption of radiation of energy.

(1) $Cl_2 \xrightarrow{h\nu} Cl_2{}^* \longrightarrow Cl + Cl$

The chlorine atoms formed react with H_2 molecules and lead to a chain reaction. These steps constitute the secondary process:

(2) $Cl + H_2 \longrightarrow HCl + H$

(3) $H + Cl_2 \longrightarrow HCl + Cl$

21.7 QUANTUM YIELD

The quantum yield ϕ for a process is defined by the equation,

$$\phi = \frac{\text{Number of molecules undergoing process } (N_m)}{\text{Number of photons absorbed } (N_p)}$$

i.e., $\phi = \dfrac{N_m}{N_p}$

This is also equivalent to

$$\phi = \frac{\text{Number of moles of a substance undergoing a process in a certain time}}{\text{Number of einsteins absorbed in the same time}}$$

or $\phi = \dfrac{n}{\epsilon}$

The number of photons absorbed is measured with a thermopile or by a chemical actinometer (a photochemical reaction for which ϕ is known).

It is obvious that the quantum yield of a primary process is always unity or less, while that for a secondary process is generally greater than one.

EXAMPLE 21.6 In the photochemical reaction between chlorine and hydrogen, 2×10^{-10} moles of chlorine have been converted into hydrochloric acid by irradiation with light of wavelength 4000 Å. What is the quantum yield of the reaction if the light energy absorbed by the system is 7.16×10^{-15} kcal ?

Solution

$$\text{Energy of one photon} = h\nu = \frac{hc}{\lambda}$$

$$h = 6.62\times10^{-34}\ \text{J s},\ c = 3\times10^{8}\ \text{m s}^{-1},\ \lambda = 4000\ \text{Å} = 4000\times10^{-10}\ \text{m}$$

$$\therefore\ \text{energy of one photon} = \frac{6.62\times10^{-34}\times3\times10^{8}}{4000\times10^{-10}} = 4.97\times10^{-19}\ \text{J}$$

$$\text{Total energy absorbed} = 7.16\times10^{-15}\ \text{kcal} = 7.16\times10^{-15}\times4.183\times10^{3} = 2.99\times10^{-11}\ \text{J}$$

$$\text{Number of photons} = \frac{2.99\times10^{-11}}{4.97\times10^{-19}} = 6.02\times10^{7}$$

$$\text{Amount of chlorine reacted} = 2\times10^{-10}\ \text{moles}$$

$$\text{Number of molecules of chlorine reacted} = 2\times10^{-10}\times6.02\times10^{23} = 12.04\times10^{13}$$

$$\text{Quantum yield, } \phi = \frac{\text{Number of chlorine molecules reacted}}{\text{Number of photons absorbed}} = \frac{12.04\times10^{13}}{6.02\times10^{7}} = 2\times10^{6}$$

21.8 PHOTOSENSITIZED REACTIONS

Certain molecules do not themselves react in the excited state, but activate molecules, which otherwise would not have absorbed light, to react. Such reactions are called *photosensitized reactions*. For example, the mercury atom absorbs light at 253.67 nm. This corresponds to about 112 kcal mol^{-1} which is more than the dissociation energy of the H—H or RC—H bond. Thus, hydrogen or methane do not absorbe this light and will not decompose when irradiated with light of 253.67 nm. However, when trace amounts of mercury vapour are present, it leads to their decomposition by the reaction,

$$\text{Hg} + h\nu = \text{Hg}^*$$
$$\text{Hg}^* + \text{H}_2 \rightarrow \text{Hg} + 2\text{H}$$

The reaction is called a *mercury sensitized reaction.* Similarly, chlorophyll acts as a sensitizer in absorbing visible light and supplying the energy for the conversion of CO_2 and water to carbohydrates. This process is called a photosynthesis:

$$\text{Chlorophyll} + h\nu \longrightarrow \text{Chlorophyll}^*$$

$$CO_2 + H_2O \xrightarrow{\text{chlorophyll}^*} \frac{1}{6} C_6H_{12}O_6 + O_2$$

21.9 SOME TYPICAL PHOTOCHEMICAL REACTIONS

As mentioned earlier, there are a wide variety of photochemical reactions:

Molecular Reactions

In these reactions, molecules absorb light and are directly converted into the products unimolecularly. These include cis–trans conversion, elimination reactions, etc.

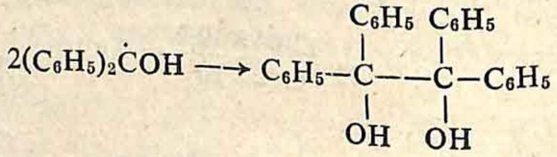
$$\textit{cis}\text{-cinnamic acid} \xrightarrow{h\nu} \textit{trans}\text{-cinnamic acid}$$

$$C_2H_5I \xrightarrow{h\nu} C_2H_4 + HI$$

There are a second category of reactions in which the excited molecules may react with other molecules. These include hydrogen abstraction, dimerization and redox reactions:

$$(C_6H_5)_2CO \xrightarrow{h\nu} (C_6H_5)_2CO^*$$

$$(C_6H_5)_2CO^* + RH \longrightarrow (C_6H_5)_2\dot{C}OH + \dot{R}$$



$$2(C_6H_5)_2\dot{C}OH \longrightarrow C_6H_5-\underset{OH}{\overset{C_6H_5}{\underset{|}{\overset{|}{C}}}}-\underset{OH}{\overset{C_6H_5}{\underset{|}{\overset{|}{C}}}}-C_6H_5$$

Chain Reactions

In these reactions, the primary photochemical reaction produces free radicals. These start chain reactions and the quantum yield can be very high, e.g.

$$Cl_2 \xrightarrow{h\nu} 2Cl$$

$$Cl + H_2 \longrightarrow HCl + H$$

$$H + Cl_2 \longrightarrow HCl + Cl$$

$$Cl + Cl \longrightarrow Cl_2$$

This reaction has a quantum yield of the order 10^6. On the other hand, for the decomposition of HI, the quantum yield is only two.

$$HI \xrightarrow{h\nu} H + I$$

$$H + HI \longrightarrow H_2 + I$$
$$I + I \longrightarrow I_2$$

The low quantum yield of this reaction is because of the fact that the I atom is relatively unreactive and does not participate in the chain propagation step.

Photochromic Reactions

In these reactions, certain molecules, when they absorb light, are converted into the conjugated isomers which are coloured. This is called photochromism. It has led to the industrial manufacture of glasses which become darker on exposure to light and hence control light transmission:

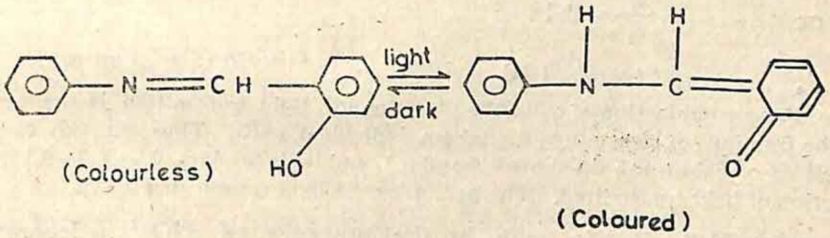


FIG. 21.3 *An example of photochromic reaction*

21.10 LASERS AND MASERS

Generally, when a beam of light is passed through a medium, it losei ts intensity. However, if there are more molecules of the medium in the excited state than in the ground state (population inversion), stimulated emission can occur and the light beam gains intensity. This is called laser action and it leads to the production of intense, coherent, monochromatic beam of light. The name *LASER* is the acronym for *Light Amplification by Stimulated Emission of Radiation*. Similarly, if the radiation is in the microwave region, it is called *MASER*. This is the acronym for *Microwave Amplification by Stimulated Emission of Radiation*.

A light beam is coherent when the light waves are in phase. The primary requirement is population inversion. This is achieved in a number of ways. In optical pumping, the molecules are excited by irradiation to the S_1 state which, by intersystem crossing, goes to a T_1 state. This gives stimulated emission. Excitation is also possible due to the energy released in chemical reactions. Lasers working on this principle are called chemical lasers.

MISCELLANEOUS EXAMPLES

Example 21.7 What percentage of light will be transmitted through two cells put together in the path of light, if their individual transmissions are 60% and 30% ?

Solution

$$D_1 = \log\frac{I_0}{I} = \log\frac{100}{60} = 0.22$$

$$D_2 = \log\frac{100}{30} = 0.52$$

$$D = D_1 + D_2 = 0.74$$

or $$\log\frac{I_0}{I} = 0.74$$

or $$\frac{I}{I_0} = 0.18$$

$\therefore$ light transmitted = 18%

Note: For a combination of cells, the fraction of light transmitted is the product of the fractions of transmitted light from individual cells. Thus, in this case, the fractions of light transmitted are 0.6 and 0.3, and their product, $0.6\times0.3=0.18$, is the fraction of light transmitted. The percentage of light transmitted is 18%.

Example 21.8 Oxalic acid, in the presence of UO_2^{2+}, decomposes according to the equation,

$$UO_2^{2+} + h\nu \longrightarrow (UO_2^{2+})^*$$

$$(UO_2)^{2+} + (COOH)_2 \longrightarrow UO_2^{2+} + CO_2 + CO + H_2O$$

by absorbing light from 250 to 450 nm. The reaction is used in chemical actinometry by estimating the amount of decomposed oxalic acid and knowing that the quantum yield for the reaction is 0.5. One litre of a 0.005 M oxalic acid solution was irradiated with light of 310 nm in presence of UO_2^{2+} ion. 20 ml of the irradiated solution, on titration, required 25 ml of 0.05 N $KMnO_4$. How many photons are absorbed per second by the solution irradiated for 10.5 min ?

Solution The normality N_1 of oxalic acid after irradiation can be calculated from the equation,

$$N_1 V_1 = N_2 V_2$$

or $$N_1 = \frac{N_2 V_2}{V_1}$$

$N_2 = 0.005$ N, $V_2 = 25$ ml, $V_1 = 20$ ml

$$N_1 = \frac{0.005\times25}{20} = 0.00625 \text{ N}$$

Now, 0.00625 N oxalic acid = 0.003125 M oxalic acid

In one litre, the number of moles reacted

= Initial molarity − Final molarity

$= 0.005 - 0.003125 = 0.001875 \text{ mol}^{-1}$

Quantum yield, $\phi = 0.5$

Number of einsteins used $= \dfrac{0.001875}{0.5} = 0.00375$

Number of photons absorbed $= 0.00375 \times 6.02 \times 10^{23}$

$= 0.0226 \times 10^{23}$

Time = 10.5 min = 630 s

Number of photons absorbed per second $= \dfrac{0.0226 \times 10^{23}}{630}$

$= 3.59 \times 10^{18}$

EXAMPLE 21.9 The average solar energy in Delhi per day (nearly 500 min) is $4.6 \times 10^7 \text{ J m}^{-2}$ per day. How many photons are falling per cm² per second if light on the average may be considered at $\lambda = 556$ nm (light of maximum visibility) ?

Solution

Energy of a photon $= \dfrac{hc}{\lambda}$

$= \dfrac{6.62 \times 10^{-34} \text{ J s} \times 3 \times 10^8 \text{ m s}^{-1}}{556 \times 10^{-9} \text{ m}}$

$= 3.57 \times 10^{-19}$ J

Energy falling per day per m² $= 4.6 \times 10^7$ J

Energy falling per second per cm² $= \dfrac{4.6 \times 10^7}{500 \times 60 \times 10{,}000} = 0.153$ J

Number of photons falling per cm² per second

$= \dfrac{\text{Energy falling per cm}^2 \text{ per second}}{\text{Energy of one photon}}$

$= \dfrac{0.153}{3.57 \times 10^{-19}}$

$= 4.28 \times 10^{17}$

QUESTIONS

Numerical Problems

21.1 (SI Units) A source of light emits radiation from 290 nm to 700 nm. Calculate the energy in einsteins at the two extreme wavelengths.

21.2 A 10 cm long cell is filled with 0.002 M $KMnO_4$ solution and absorbs 20% of incident light. What should be the concentration of the solution if it absorbs 80% of incident light ?

21 3 Calculate the value of an einstein of energy in kJ mol^{-1} for radiation of

(i) wavelength 4000 Å

(ii) frequency 2×10^{13}

21.4 Monochromatic light was passed through a cell of 1 cm thickness containing 1×10^{-4} M of a given substance. The absorbance was found to be 0.15 (after correcting for absorbance of the solvent). Calculate the molar extinction coefficient.

21.5 How much energy is required by the sodium atom to emit D-line of wavelength 5890 Å ?

21.6 A cell of 1 cm path length containing 0.01 M $Cr_2(SO_4)_3$ solution transmits 60% of light at 340 nm. What is the extinction coefficient of the salt ? What should be the concentration of the salt so that the transmission of light is 30% ?

21.7 Calculate the energy of one photon of light of wavelength 4900 Å. Will it be able to dissociate a bond in a diatomic molecule which absorbs this photon and has a bond energy equal to 72 kcal mol^{-1} ?

21.8 Acetone can be photolysed by irradiating it with light of $\lambda = 310$ nm according to the reaction,

$$(CH_3)_2CO \rightleftharpoons C_2H_6 + CO$$

In an experiment, the vessel containing acetone absorbs 10^{-3} J s^{-1} and yields 3×10^{14} CO molecules per second. What is the quantum yield for the reaction ?

21.9 A thermopile receives monochromatic light ($\lambda = 380$ nm) over an area of 0.5 cm^2 and its temperature rises by 10^{-3} s^{-1} (assuming no loss of heat). What is the flux of light falling on the thermopile (the heat capacity of the thermopile is 3.5 J K^{-1}) ?

21.10 The quantum yield for a chemical reaction, with light of wavelength ranging from 340 to 500 nm, is nearly constant. Which of the following

(a) $\lambda = 410$ nm

(b) $\bar{\nu} = 25{,}000$ cm^{-1}

(c) $\nu = 4.2 \times 10^{14}$ s^{-1}

will be more economical from the energy point of view ? If the spectral distribution of the lamp at 410 nm, 25000 cm^{-1} and 4.2×10^{14} s^{-1} is 8%, 10% and 20% of energy, which light is more economical to use ?

21.11 A one-litre flask containing HI in the gaseous state absorbs 3.42×10^{21} quanta, with the production of 5.53×10^{-3} moles of iodine. What is the quantum yield of the reaction ?

21.12 When a sample of acetone was irradiated with a certain monochromatic light at the rate of 8.5 quanta per second, the quantum yield for the decomposition was found to be 0.25 molecule per quantum. Calculate the number of moles of acetone decomposed in one hour.

21.13 The extinction coefficient of a substance in a solution is 100 cm^2 mol^{-1}. What should be its minimum concentration so that, when kept in a cell of 1 cm path length, it absorbs 99% of light ?

21.14 What is the optical density of a solution which absorbs two-thirds of the incident light ?

21.15 Two cells with optical densities 0.3010 and 0.6020 are put together in a photochemical experiment. What is the percentage of the initial light transmitted by them.

QUIZ QUESTIONS

Type A: Multiple Choice

21.16 A molecule returns from the excited singlet state to the ground singlet state with emission of light. The process is known as

(a) fluorescence

(b) phosphorescence

(c) chemiluminescence

(d) scattering

21.17 A molecule goes from the excited singlet state to the triplet state without emitting light. The process is known as
(a) inter-system crossing
(b) fluorescence
(c) internal conversion
(d) phosphorescence

21.18 When a transition between [states of the same multiplicity occurs without emitting light, the process is called
(a) fluorescence
(b) quenching
(c) internal conversion
(d) intersystem crossing

21.19 A molecule returns from the first excited triplet state to the ground state singlet. The light emitted is known as
(a) inter-system crossing
(b) fluorescence
(c) phosphorescence
(d) quenching

21.20 The quantum yield of a photochemical reaction is
(a) always less than unity
(b) always equal to unity
(c) always greater than unity
(d) can have any value $\geqslant 0$ depending on the reaction

21.21 According to the Grotthus–Draper law,
(a) only absorbed light is effective in producing photochemical changes
(b) only light between certain wavelengths is effective in photochemical changes
(c) light is effective only for photochemical reactions in solution
(d) the light absorbed is proportional to its intensity

21.22 Which of the following statements is correct ?
(a) The wavelength of phosphorescence is less than the wavelength absorbed
(b) The transition from T_1 to S_0 without the emission of light is called phosphorescence.
(c) The combination of CO_2 and water in plants, in the presence of chlorophyll, is an example of bioluminescence.
(d) Population inversion is a necessary condition for laser action.

21.23 The wavelength of fluorescent light (λ_f) is related to the wavelength of the absorbing light (λ_{ab}) by
(a) $\lambda_f > \lambda_{ab}$
(b) $\lambda_f < \lambda_{ab}$
(c) $\lambda_f \propto \lambda_{ab}$
(d) $\lambda_f \propto 1/\lambda_{ab}$

21.24 The value of an einstein
(a) is independent of wavelength
(b) decreases with increase in wavelength
(c) increases with increase in wavelength
(d) depends on the temperature of the absorbing system

21.25 The extinction coefficient has the units
(a) $cm^2\ mol^{-1}$
(b) $cm^3\ mol^{-1}$
(c) $mol\ cm^{-2}$
(d) $mol\ cm^{-3}$

21.26 The Lambert–Beer law states that
(a) transmission is directly proportional to path length
(b) transmission is directly proportional to concentration

(c) absorbence is inversely proportional to transmission
(d) absorbence is directly proportional to concentration

21.27 Reactions in which molecules absorbing light do not themselves react but induce other molecules to react are called
(a) chain reactions
(b) photosensitized reactions
(c) reversible reactions
(d) free radical reactions

21.28 "Only those radiations which are absorbed by the system can bring about chemical change." This is a statement of the
(a) Beer–Lambert law
(b) Grotthus-Draper law
(c) Einstein law
(d) photochemical equivalence law

21.29 The reverse of a photochemical reaction is called
(a) phosphorescence
(b) chemiluminescence
(c) fluorescence
(d) photosensitization

21.30 The quantity $c\epsilon x$ is called (where c is concentration, ϵ extinction coefficient, and x path length)
(a) optical density
(b) molar absorption coefficient
(c) extinction coefficient
(d) absorption coefficient

Type B: Multiple Choice (Numerical Problems)

21.31 An einstein of light of $\lambda = 350$ nm passing through a solution of oxalic acid in the presence of UO_2^{2+} reduces the concentration of oxalic acid from 2 M to 1 M in 500 ml of solution. The quantum yield of the photochemical reaction is
(a) 1
(b) 0.5
(c) 2
(d) 0.35

21.32 500 ml of 0.1 M ferrioxalate solution is irradiated with light $\lambda = 310$ nm. A litre of the solution absorbs 0.02 einstein of light and the quantum yield of the reaction is 1.25. What is the concentration of Fe^{3+} ion in the solution?
(a) 0.025
(b) 0.0125
(c) 0.050
(d) 0.002

21.33 The extinction coefficient of $K_3[Fe(CN)_6]$ is 1000 $cm^2\ mol^{-1}$. The concentration of $K_3[Fe(CN)_6]$ solution, if placed in a cell of 5 cm path length having optical density equal to 0.5 is
(a) 10^{-4} M
(b) 10^{-3} M
(c) 0.5×10^{-4} M
(d) 0.5×10^{-3} M

21.34 The quantum yield for the decomposition of HI is 2. If in an experiment, 0.01 moles of HI are decomposed, the number of photons absorbed is equal to
(a) 6.02×10^{21}
(b) 3.01×10^{21}
(c) 12.04×10^{21}
(d) 3.01×10^{23}

21.35 The optical density of a solution, with reference to the solvent, is 0.3. The extinction coefficient of the solute is 3000 and the cell length is 10 cm. The concentration of the solute is

(a) 1×10^{-5} M (b) 0.3 M
(c) 1×10^{-3} M (d) 1×10^{-4} M

Type C: True or False

21.36 The amount of light absorbed is directly proportional to the concentration of the absorbing species.

21.37 Only the light absorbed by the system is effective in bringing about a photochemical reaction.

21.38 An einstein has the same value for radiations of all wavelengths.

21.39 The quantum yield of a primary process cannot be greater than unity.

21.40 Each molecule taking part in a chemical reaction induced by absorption of radiation takes up only one quantum of the radiation causing the reaction.

21.41 The radiation emitted when a transition occurs between states of different multiplicity, such as T_1 to S_0, is called phosphorescence.

21.42 The state in which two electrons have the same spin is called the singlet state.

21.43 In intersystem crossing, the system goes from the singlet into the triplet state, or vice versa, without the emission of radiation.

21.44 Secondary photochemical reactions may have quantum yields greater than unity.

21.45 The triplet state generally has lower energy than the singlet state, for a given electronic configuration.

Type D: Fill in the Blanks

21.46 Fluorescence is the process of an excited state returning to the ground state of the same ———— with the emission of light.

21.47 Phosphorescence is the process of the triplet excited state returning to the ———— ground state with the emission of light.

21.48 The wavelength of the fluorescent radiation is generally ———— than the wavelength of the light absorbed.

21.49 The units of the extinction coefficient are ————.

21.50 Reactions in which the molecules absorbing light do not react themselves but can induce other molecules to react are called ———— reactions.

21.51 ———— is equal to log (I_0/I).

21.52 The lower the wavelength of light the ———— is the value of einstein corresponding to it.

21.53 Quantum yield is the ratio of the number of moles consumed in a process and the number of ———— absorbed by it.

21.54 In radiationless transfer, if the transition occurs between states of the same multiplicity, it is called ———— and between states of different multiplicity, ————.

21.55 The emission of light in a chemical reaction is called ————.

ANSWERS

Numerical Problems

21.1 412.4 kJ, 171 kJ *21.2* 2.93×10^{-3} M *21.3* (i) 298.9 kJ (i) 7.97 kJ *21.4* 1.5×10^{3} *21.5* 203 kJ *21.6* 0.0236 M *21.7* Bond will not be broken *21.8* 0.19

21.9 1.339×10^{16} cm^{-2} s^{-1} *21.10* 4.2×10^{14} s^{-1}, 25000 cm^{-1} *21.11* 1.95 *21.12* 1.02 mol *21.13* 1/50 M *21.14* 0.476 *21.15* 12.50%.

Quiz Questions

21.16 (a) *21.17* (a) *21.18* (c) *21.19* (c) *21.20* (d) *21.21* (d) *21.22* (a) *21.23* (a) *21.24* (b) *21.25* (a) *21.26* (d) *21.27* (b) *21.28* (b) *21.29* (b) *21.30* (a) *21.31* (b) *21.32* (c) *21.33* (a) *21.34* (b) *21.35* (a) *21.36* False *21.37* True *21.38* False *21.39* False *21.40* True *21.41* True *21.42* False *21.43* True *21.44* True *21.45* True *21.46* multiplicity *21.47* singlet *21.48* higher or greater *21.49* cm^2 mol^{-1} *21.50* photosensitized *21.51* optical density *21.52* greater *21.53* einstein *21.54* internal conversion, intersystem crossing *21.55* chemiluminescence.

22

Adsorption and Heterogeneous Catalysis

The atoms or molecules on the surface of a solid or liquid are in a higher energy state than those in the bulk. As a result, these have a tendency to interact and retain molecules of other species which come in contact with them. The enrichment of chemical substances at the surface of a solid or liquid is called *adsorption*. Adsorption studies are very important for understanding reactions taking place on surfaces. A number of purification processes in the chemical industry, gas chromatography and pollution control techniques are based on the adsorption phenomenon.

22.1 ADSORPTION AND ABSORPTION

Adsorption is limited to the surface only, while in absorption the molecules of the absorbed substances are dispersed throughout the bulk. McBain proposed the common term *sorption* for both these phenomena.

The substance on whose surface adsorption takes place is called the *adsorbent* and the substance that gets adsorbed is called the *adsorbate*. The adsorbent may be a solid or liquid, and the adsorbate can be a gas or a solute in some solution. The quantity of a substance adsorbed per gram of the adsorbent can be expressed either in terms of the mass of the adsorbate or the number of moles of the adsorbate, or the volume of the adsorbate if it is a gaseous substance. The volume may be expressed under ambient conditions (p and T at which adsorption studies have been made) or the volume be reduced to STP for quantitative comparison of adsorption studies at different temperatures and pressures.

EXAMPLE 22.1 Three gram of oxygen is adsorbed on 1.2 g of metal powder at 300 K and 0.7 atm. Express the mass, number of moles, and volume of oxygen (at 300 K, 0.7 atm and at S.T.P.) adsorbed per gram of the adsorbent.

Solution

Mass of adsorbate, $x=3$ g
Mass of adsorbent, $m=1.2$ g

Mass of adsorbate per gram of adsorbent$=\frac{x}{m}=\frac{3}{1.2}=2.5$

Number of moles of adsorbate per gram of adsorbent$=\frac{2.5}{32}=0.078$

Volume of 2.5 g of O_2 at 300 K and 0.7 atm$=\frac{2.5}{32}\times\frac{82\times300}{0.7}$

$$=2745.5 \text{ cm}^3$$

Volume of 2.5 g of O_2 at 273 K and 1 atm$=\frac{2.5}{32}\times\frac{82\times273}{1}$

$$=1748.9 \text{ cm}^3$$

Therefore, $\frac{v}{m}$ (300 K, 0.7 atm)$=2745.5 \text{ cm}^3 \text{ g}^{-1}$

$$\frac{v\text{ (STP)}}{m}=1748.9 \text{ cm}^3 \text{ g}^{-1}$$

22.2 PHYSICAL ADSORPTION (PHYSISORPTION) AND CHEMISORPTION

Molecules of the adsorbate are held to the surface by van der Waals type of interactions, in physical adsorption. The term physisorption has been proposed recently for physical adsorption. The heat of physisorption is of the order of the heat of condensation of vapours into liquids. Adsorption generally decreases with increase of temperature and the activation energy for physical adsorption is nearly zero. If the adsorbate is in the gaseous state and the studies are carried out below its critical temperature, then adsorption increases rapidly near its critical pressure—indicating the onset of condensation.

Chemisorption, on the other hand, involves a chemical reaction between adsorbed molecules and the molecules (or atoms) of the adsorbent on the surface. The heat of chemisorption is of the same order of magnitude as of chemical reaction. Like chemical reaction, there are activation energies for chemisorption. Therefore, the rate of chemisorption increases with increase of temperature, although the amount of a substance chemisorbed at equilibrium decreases with increase of temperature as for any other exothermic reaction. The state of the adsorbent molecule may be quite different from that in the bulk. For example, oxygen exists as O_2 in bulk, but on the surface it may be present as O_2^-, O_2^{2-}, O, O^- O^{2-}, etc.

EXAMPLE 22.2 (SI Units) The activation energy and enthalpy of chemisorption of oxygen on a metal surface is 37.3 kJ mol^{-1} and -72.1 kJ mol^{-1}. At a certain pressure, the rate constant for chemisorption is 1.2×10^{-3} s^{-1} and x/m is 2.5 g per gram of adsorbent at 318 K. What will be the value of the rate constant and x/m at 308 K ?

Solution

$$k \text{ (rate constant)} = A\, e^{-Ea/RT}$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or
$$\ln k_2 = \ln k_1 + \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Now, $T_1 = 318$ K, $E_a = 37.3$ kJ mol^{-1} and
$T_2 = 308$ K

$$\log k_2 = \log(1.2\times10^{-3}) + \frac{37300}{8.31\times2.303}\left(\frac{1}{318} - \frac{1}{308}\right)$$

$$= -2.9208 - \frac{37300\times10}{8.31\times2.303\times318\times308} = -2.9208 - 0.1989$$

$$k_2 = 7.6\times10^{-4}\ \text{s}^{-1}$$

It can be seen that the rate constant, and hence the rate of chemisorption, decreases with decrease of temperature.

Now, like an equilibrium constant,

$$\frac{x}{m} = e^{-\frac{\Delta S}{R}}\, e^{-\frac{\Delta H}{RT}}$$

$$\ln \frac{\left(\frac{x}{m}\right)_{T_2}}{\left(\frac{x}{m}\right)_{T_1}} = \frac{\Delta H}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or
$$\log\left(\frac{x}{m}\right)_{T_2} = \log\left(\frac{x}{m}\right)_{T_1} + \frac{\Delta H}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

Now $T_1 = 318$ K, $\Delta H = -72.1$ kJ and $T_2 = 308$

$$\log\left(\frac{x}{m}\right)_{308} = \log(2.5) - \frac{72100}{2.303\times8.31}\left[\frac{1}{318} - \frac{1}{308}\right]$$

$$= \log(2.5) + \frac{72100\times10}{2.303\times8.31\times318\times308}$$

$$\log\left(\frac{x}{m}\right)_{308} = 0.3979 + 0.3846 = 0.7825$$

$$\left(\frac{x}{m}\right)_{308} = 6.06 \text{ g per gram of adsorbent}$$

It can be seen that the amount of oxygen adsorbed is much more at equilibrium although the rate of chemisorption decreases. Thus, both kinetic and equilibrium factors are important for industrial processes where the maximum yield is desired at a reasonable rate.

22.3 CHARACTERISTICS OF ADSORPTION BY SOLIDS

(a) x/m depends on the chemical nature of both the adsorbent and adsorbate, and their physical state.

(b) x/m also depends on the equilibrium concentration or pressure of the adsorbate, and the temperature.

(c) Adsorption is generally reversible.

(d) Adsorption is generally accompanied by decrease in enthalpy and entropy. The two factors have opposing effects on the Gibbs free energy for the chemisorption.

(e) Adsorption can be highly selective, i.e. the given adsorbent may adsorb preferentially over a particular adsorbate.

22.4 ADSORPTION ISOTHERM

A relation between x/m and the equilibrium concentration (solution) or pressure (gas) of the adsorbate at a fixed temperature is called the *adsorption isotherm*. This may be obtained experimentally by determining x/m as a function of C (or p). It has been found from experience that the adsorption data can be fitted to some empirical relation called the adsorption isotherm. The most common types are discussed below.

22.5 FREUNDLICH ADSORPTION ISOTHERM

The Freundlich adsorption isotherm is represented by the equation:

$$\frac{x}{m} = k\,C^n \qquad \text{(for solutions)} \qquad (22.1a)$$

or

$$\frac{x}{m} = k\,p^n \qquad \text{(for gases)} \qquad (22.1b)$$

The parameters k and n depend upon the nature of the adsorbent and the adsorbate and can be determined by plotting $\log (x/m)$ against $\log C$ (or $\log p$). This should be a straight line with the slope equal to n and the intercept equal to $\log k$. The value of n is generally less than one, and hence x/m tends to level off as C or p increases.

22.6 LANGMUIR ADSORPTION ISOTHERM

The adsorption isotherm (Fig. 22.1a) is represented by the relation

$$\frac{x}{m} = \frac{ap}{1+bp} \qquad (22.2)$$

is known as the Langmuir adsorption isotherm and, at very high pressure, it acquires the limiting form

$$\frac{x_0}{m} = \frac{a}{b} \tag{22.3}$$

when x_0/m becomes constant, i.e. a given adsorbent cannot adsorb more than x_0/m of the adsorbate according to this equation. In order to determine the parameters a and b Eq. (22.2), the equation may be written in its inverse form:

$$\frac{m}{x} = \frac{1+bp}{ap} = \frac{b}{a} + \frac{1}{ap}$$

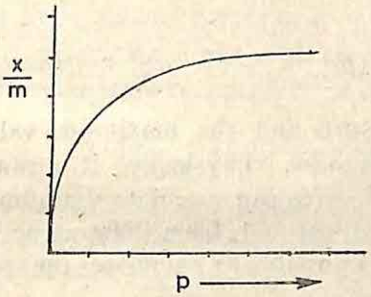


FIG. 22.1a *Langmuir adsorption isotherm*

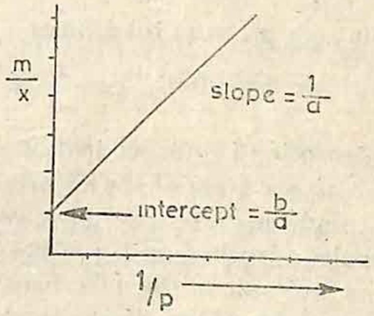


FIG. 22.1b *A plot of m/x against 1/p gives a straight line with slope = 1/a and intercept = b/a*

A plot of m/x against $1/p$ gives a straight line (Fig. 22.1b) with slope and intercept equal to $1/a$ and b/a, respectively. Thus, both parameters can be determined.

Equation (22.2) was first derived by Irving Langmuir. He assumed:

(a) The surface is uniform, i.e. all molecules are adsorbed with the same enthalpy and entropy of adsorption and there is no interaction between the adsorbed molecules.

(b) Only a unimolecular adsorbed layer is formed. At equilibrium, two opposing processes, viz. adsorption of molecules from the gas phase and desorption of the adsorbed molecules, have equal rates. If p is the equilibrium pressure of the adsorbate and θ ($= x/x_0$) is the fraction of the surface covered by them,

$$\text{Rate of adsorption} = k_1\,(1-\theta)\,p \tag{22.4}$$

$$\text{Rate of desorption} = k_2\,\theta \tag{22.5}$$

At equilibrium, $k_2\,\theta = k_1\,(1-\theta)\,p = k_1\,p - k_1\,\theta\,p$

or
$$\theta = \frac{k_1 p}{k_2 + k_1 p} = \frac{\frac{k_1}{k_2}p}{1+\frac{k_1}{k_2}p} = \frac{bp}{1+bp} \tag{22.6}$$

but
$$\theta = \frac{x}{x_0} = \frac{x/m}{x_0/m} = \frac{bp}{1+bp} \tag{22.7}$$

For a given experiment, x_0/m is constant and (22.7) may be rewritten as

$$\frac{x}{m} = \frac{\frac{x_0}{m}\,bp}{1+bp} = \frac{ap}{1+bp} \tag{22.8}$$

The equation is identical to eq. (22.2). It also tells us that $(b = k_1/k_2)$ is an equilibrium constant and a is proportional to the equilibrium constant. At low pressures, it reduces to

$$\frac{x}{m} = ap \tag{22.9}$$

and at high pressure it becomes

$$\frac{x_0}{m} = \frac{a}{b} = \frac{a}{b}\,(p)^0 \tag{22.3}$$

i.e. adsorption is independent of pressure and the maximum value of adsorbate per gram of the adsorbent is x_0/m. Physically, it means that $\theta = 1$ and the surface is fully covered. We can calculate the number of molecules adsorbed on 1 g of the adsorbent and, from the area occupied by one molecule of the adsorbate, it is possible to calculate the surface area per gram of the given adsorbent.

Example 22.3 The adsorption of nitrogen on a metal powder obeys the Langmuir equation. The following experimental results have been obtained.

p (torr)	1	5	10	30	70	150
x/m	0.75	1.50	1.71	1.89	1.95	1.98

Determine the parameters a and b of the Langmuir equation and also find the maximum number of molecules adsorbed by 1 g of the adsorbent. If the area occupied by N_2 molecules is 16 Å², determine the surface area of metal per gram.

Solution We first calculate m/x and $1/p$:

m/x	1.333	0.666	0.585	0.529	0.513	0.505
$1/p$ (torr^{-1})	1	0.2	0.1	0.033	0.014	0.0066

when m/x is plotted against $1/p$, we get slope $= 0.83$ torr and intercept $= 0.5$. Hence,

$$1/a = 0.83 \text{ torr} \qquad \text{or} \qquad a = 1.2 \text{ torr}^{-1}$$

$$b/a = 0.5 \qquad \text{and} \qquad b = 0.6 \text{ torr}^{-1}$$

It may be noted that $x_0/m = b/a = 0.5$, i.e. 0.5 g of nitrogen is adsorbed per gram of metal powder

$$\text{Number of moles of nitrogen adsorbed per g of metal powder} = \frac{0.5}{28} = 0.01786 \text{ mol}$$

Number of molecules of N_2 adsorbed per gram of metal powder $= 0.01786 \times 6.02 \times 10^{23}$

$= 1.07 \times 10^{22}$ molecules

Surface area of metal $= 16 \times 1.07 \times 10^{22}$ Å^2 g^{-1}

$= 16.12 \times 10^{22}$ Å^2 g^{-1}

$= 16.12 \times 10^{6}$ cm^2 g^{-1}

$= 16.12 \times 10^{2}$ m^2 g^{-1}

The Langmuir equation for solution becomes

$$\frac{x}{m} = \frac{ac}{1+bc} \tag{22.10}$$

The units of a and b depend on the units of c and x (x can be in g, and g moles) as the units of m are always g. The following representation of the equation is used quite often:

$$\theta = \frac{x}{x_0} = \frac{v}{v_0} = \frac{bp}{1+bp} \tag{22.11}$$

where v and v_0 are the volumes (reduced to the same p and T) of the gas adsorbed at pressure p and the limiting high pressure. Equation (22.11) is generally used in the form

$$\frac{1}{v} = \frac{1}{v_0} + \frac{1}{v_0\, bp} \tag{22.12}$$

If v is the volume of gas adsorbed per gram of the adsorbent then $1/v_0$ is the intercept for the straight line of $1/v$ vs $1/p$.

EXAMPLE 22.4 At what value of p is $\theta = 0.5$ in Example 22.3. The value of b calculated in Example 22.3 $= 0.6$ torr^{-1}. Now, using Eq. (22.11)

$$\theta = \frac{bp}{1+bp}$$

Putting $\theta = 0.5$ and $b = 0.6$ torr^{-1}

We get $0.5 = \dfrac{0.6\,p}{1+0.6\,p}$

$0.5 + 0.3\,p = 0.6\,p$

or $\quad p = \dfrac{0.5}{0.3} = 1.66$ torr

22.7 OTHER ADSORPTION ISOTHERMS

The Langmuir equation could explain only the simple isotherm (Fig. 22.1). However, four other general types of isotherms have been observed in the adsorption of gases on solids (Figs. 22.2 and 22.3).

The isotherms of Types II and III were explained on the basis of multilayer adsorption. Brunauer, Emmett and Teller proposed that the

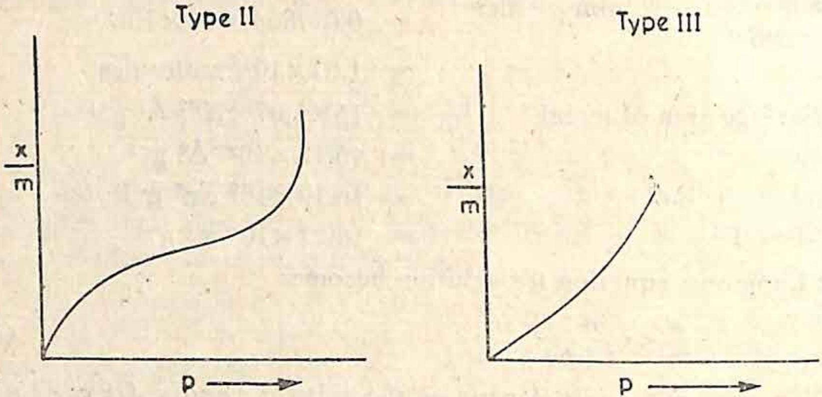


FIG. 22.2 *Adsorption isotherms of types II and III*

adsorption involves the formation of multi-molecular layers on the surface. They derived an equation (called B.E.T. equation)

$$\frac{p}{v\,(p^0-p)}=\frac{1}{v_0\,C}+\left(\frac{C-1}{v_0\,C}\right)\frac{p}{p_0} \qquad (22.13)$$

where v is the volume (reduced to standard conditions) of gas adsorbed at pressure p and temperature T, p^0 is the saturated vapour pressure of the adsorbate at the given temperature of adsorption, v_0 is the volume of gas adsorbed in making a unimolecular layer and C is a constant. If we plot $p/[v(p^0-p)]$ against, p/p_0. we get a straight line with slope and intercept equal to $\frac{C-1}{v_0\,C}$ and $\frac{1}{v_0\,C}$ respectively from which the values of v_0 and C can be calculated. The value of v_0 can be used for determining the surface area of the adsorbent. For curve II, $E_1 > E_L$, where E_1 is the heat of adsorption of the first layer and E_L is the heat of liquefaction of the gas. For the isotherm of type II, $E_1 < E_L$.

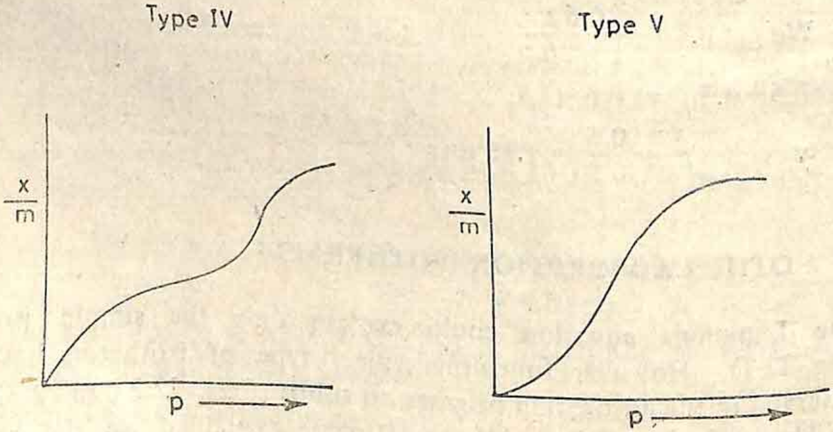


FIG. 22.3 *Adsorption isotherms of types IV and V*

In addition, isotherms of types IV and V were observed. In these cases it was suggested that, in addition to the formation of multilayer adsorption, the gas gets condensed in the pores and capillaries of the adsorbent. For an isotherm of the type IV, $E_1 > E_L$, and for the type V, $E_1 < E_L$.

EXAMPLE 22.5 The adsorption of butane over 2 g of metal catalyst has been studied at 273 K and the following results have been obtained:

Eq. pressure p (torr)	56.4	89.5	125.2	156.6	179.3	187.5
Volume of gas adsorbed at S.T.P. v(S.T.P.)	18.22	21.98	25.31	27.81	29.61	30.17

If the area occupied by butane molecule is 44.5 Å² and its saturation pressure at 273 K is 774.4 torr, calculate the surface area per gram of the catalyst.

Solution We apply the B.E.T. equation

$$\frac{p}{v(p^0-p)} = \frac{1}{v_0 C} + \left(\frac{C-1}{v_0 C}\right)\frac{p}{p_0}$$

We have to plot $\dfrac{p}{v\ (p^0-p)}$ against $\dfrac{p}{p_0}$,

we calculate both quantities

$\dfrac{p}{v\,(p^0-p)} \times 10^3$	4.31	5.95	7.62	9.11	10.18	10.59
$\dfrac{p}{p_0} \times 10^2$	7.28	11.56	16.17	20.22	23.15	24.21

The plot of $\dfrac{p}{v\,(p^0-p)}$ and $\dfrac{p}{p_0}$ gives a straight line with intercept $\dfrac{1}{v_0 C} = 1.35 \times 10^{-3}$. From these we obtain $C = 22.05\ \text{cm}^{-3}$ and $v_0 = 26.13$ cm³. This is for 2 g of catalyst. For 1 g, the monolayer is formed by $\dfrac{26.13}{2} = 13.065\ \text{cm}^3 = \dfrac{13.065}{22400}$ mol.

$$\text{Number of molecules of } C_4H_{10} = \frac{13.065}{22400} \times 6.02 \times 10^{23} = 3.51 \times 10^{20}$$

$$\begin{aligned}\text{Area per gram} = 44.5 \times 3.51 \times 10^{20}\ \text{Å}^2 &= 15.6 \times 10^{21}\ \text{Å}^2 \\ &= 15.6 \times 10^{5}\ \text{cm}^2\ \text{g}^{-1}.\end{aligned}$$

22.8 ADSORPTION FROM SOLUTIONS

Solids can adsorb dissolved substances from solutions also. Common examples are the adsorption of colouring impurities by activated charcoal in decolourizing of solutions.

Adsorption from solutions generally follows the equation proposed by Freundlich. This may be expressed as

$$\frac{x}{m} = kC^n \tag{22.1}$$

where $\frac{x}{m}$ is the amount of solute absorbed, per gram of absorbent, from a solution of concentration C, at a given temperature, and k and n are constants for the given adsorbent and solute. The value of n is less than unity.

22.9 ADSORPTION FROM MULTI-COMPONENT ADSORBATE

If the adsorbate consists of two or more than two components, there is competition between these components to occupy the surface. If all the components obey the Langmuir adsorption isotherm, their b will be different and the fraction of the surface θ_i occupied by component i is given by

$$\theta_i = \frac{b_i\theta_i}{1+\Sigma b_i\theta_i} \tag{22.14}$$

22.10 HETEROGENEOUS CATALYSIS

There are many chemical reactions which take place only in the presence of certain solid surfaces, and occur at very slow rates in the absence of such solids. These solid substances are called *heterogeneous catalysts*. Some typical examples are:

(a) *Solid catalyst+gaseous reactant* NH_3 is synthesized from N_2 and H_2 over Fe/Mo as catalyst:

$$N_2+3H_2 \xrightarrow{\text{Fe/Mo}} 2NH_3$$

(b) *Solid catalyst+liquid reactant* The decomposition of H_2O_2 is catalysed by platinum black:

$$H_2O_2 \xrightarrow{\text{Pt black}} H_2O+\tfrac{1}{2}\,O_2$$

(c) *Solid catalyst+gaseous and liquid reactants* Oxidation of liquid hydrocarbons to carboxylic acid over cobalt bromide.

$$R-CH_3+\tfrac{3}{2}\,O_2 \xrightarrow{CoBr_2} RCOOH+H_2O$$

22.11 KINETICS OF HETEROGENEOUS REACTIONS

The reactions involving one molecule or decomposition reaction may be explained in terms of the Langmuir adsorption isotherm.

The rate of the reaction is defined by the rate at which the pressure of the reactant decreases, i.e.

$$\text{rate} = -\frac{dp}{dt}$$

If only the adsorbed species react and no product molecule is adsorbed, it should be proportional to θ, i.e.

$$\text{rate} = -\frac{dp}{dt} = k\theta = \frac{kbp}{1+bp}$$

or

$$-\frac{dp}{dt} = \frac{kbp}{1+bp} \tag{22.15}$$

Equation (22.15) is valid at all pressure. However, the kinetics of the reaction simplifies to a great extent under extreme conditions, i.e.

(a) *Very low pressure* In this case the term bp can be neglected compared to 1 in the denominator, and the equation becomes

$$-\frac{dp}{dt} = kbp \tag{22.15a}$$

i.e. the rate is proportional to the first power of p, and hence behaves like a first order reaction with the first order rate constant equal to kb.

(b) *Very high pressure* Unity can be neglected compared to bp and Eq. (22.15) reduces to

$$-\frac{dp}{dt} = k = k(p)_0 \tag{22.15b}$$

i.e. the rate becomes independent of p and a zero order reaction with rate constant $= k$.

22.12 KINETICS OF RETARDED REACTIONS

In some reactions, in addition to the reactants, products are also adsorbed on the surface. As a result, the fraction of the surface adsorbed by the reactant decreases and, therefore, the rate of the reaction decreases. Thus, a strongly adsorbed product will retard the reaction. Consider the reaction

$$\text{A} \longrightarrow \text{B} + \text{C}$$

$$\theta_A = \frac{b_A p_A}{1 + b_A p_A + b_B p_B + b_C p_C} \tag{22.16}$$

the rate of the reaction is given by

$$\text{Rate} = k\theta_A = \frac{k\theta p_A}{1 + b_A p_A + b_B p_B + b_C p_C} \tag{22.17}$$

It can be seen that adsorption of B and C will retard the reaction. However, the quantitative relation will depend on the relative values of b_i's and the partial pressures of the reactant and product molecules.

If product B is strongly absorbed compared to A and C,

$$\text{rate} = \frac{k\theta p_A}{b_B p_B} = k_0 \, p_A / p_B \tag{22.18}$$

The decomposition of NH_3 on Pt at 1138°C follows this equation as H_2 is strongly adsorbed.

If product B is moderately adsorbed but much more than A and C, the rate equation becomes

$$\text{Rate}=\frac{k\theta p_A}{1+b_B p_B} \tag{22.19}$$

The decomposition of N_2O on platinum follows Eq. (22.19).

22.13 CATALYTIC POISONS

Substances which lower the catalytic activity of a surface are called catalytic poisons. In most cases, the poisoning is due to the inhibitor or poison being preferentially adsorbed on the surface. Poisons may be of two types, temporary and permanent. In temporary poisoning, the activity of the surface decreases temporarily. As soon as the poison is removed from the presence of the catalyst the surface becomes active. On the other hand, permanent poisoning involves a chemical interaction with the surface and forms a new catalytically inert surface.

QUESTIONS

Numerical Problems

22.1 Adsorption of methane has been studied by Langmuir at 90 *k*. The following data have been obtained:

Equilibrium pressure (bar)	13.4	11.1	9.6	8.55	7.4	6.68	5.85
$\frac{x}{m}$ (cm^3 g^{-1} at S.T.P.)$\times 10^2$	8.50	8.04	7.59	7.16	6.79	6.42	6.12

Calculate the values of constants a and b in the Langmuir equation and also determine the value of v_0.

22.2 Five grams of a catalyst adsorb 400 cm^3 of nitrogen (calculated at S.T.P.) to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 Å^2.

22.3 Four grams of a substance adsorb 87.5 cm^3 of oxygen at 450 torr and at 37°C. Express $\frac{x}{m}$ in different ways $\left(\text{g g}^{-1}, \text{mole g}^{-1}, v\ (\text{S.T.P.})\ \text{g}^{-1}\right)$

22.4 Charcoal adsorbs a solute from its aqueous solution and obeys the Freundlich isotherm. The following data were obtained :

Equilibrium concentration$\times 10^2$ M	2.0	4.0	6.0	8.0
x/m	0.185	0.290	0.364	0.428

Determine the values of k and n.

22.5 For an adsorbent-adsorbate system obeying the Langmuir adsorption isotherm, $a=0.48$ bar^{-1} and $b=0.16$ bar^{-1}. At what pressure will 50% of the surface be covered ?

QUIZ QUESTIONS

Type A: Multiple Choice

22.6 The enrichment of chemical substances at the surface of a solid is called;

(a) adsorption (b) absorption
(c) sorption (d) isotherm

22.7 The substance on whose surface adsorption takes place is called the

(a) adsorbent
(b) adsorbate
(c) active substance
(d) porous substance

22.8 Which of the following characteristics of adsorption is wrong ?

(a) Adsorption on solids is reversible in nature.
(b) Adsorption, in general, increases with increase in temperature.
(c) Adsorption is generally selective in nature.
(d) Both enthalpy and entropy of adsorption are negative.

22.9 In terms of the amount of the substance adsorbed per gram of the adsorbent (x/m), and pressure p of the gas, the Freundlich adsorption isotherm is represented as

(a) $\frac{x}{m} = \frac{k}{p^n}$
(b) $\frac{x}{m} = kp^n$
(c) $p = k\left(\frac{x}{m}\right)^n$
(d) $\frac{x}{m} = \left(\frac{k}{p}\right)^n$

22.10 The Langmuir adsorption isotherm shows that the amount of adsorbed gas per gram of the solid is equal to

(a) $\frac{ap}{1+bp}$
(b) $\frac{ap+1}{1-bp}$
(c) $\frac{1+ap}{1-bp}$
(d) $a\,(1+bp)$

22.11 According to the Langmuir isotherm, when the pressure of the gas is very large, the adsorption

(a) is directly proportional to pressure
(b) is inversely proportional to pressure
(c) is directly proportional to the square of the pressure
(d) is independent of pressure

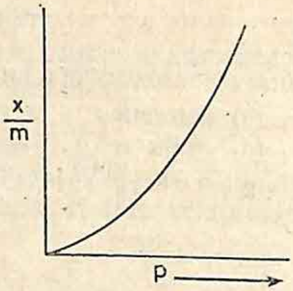
22.12 If θ is the fraction of the surface occupied by adsorbate molecules at equilibrium, then, according to the Langmuir theory, the rate of condensation is given by

(a) $a\,\theta$ (b) $a\,\theta\,p$
(c) $a\,(1-\theta)\,p$ (d) $a\,(1-\theta)$

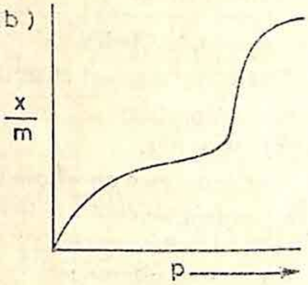
where a is a constant.

22.13 Which of the following isotherms was successfully explained by the Langmuir unimolecular layer theory ?

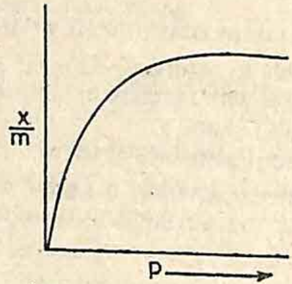
(a)



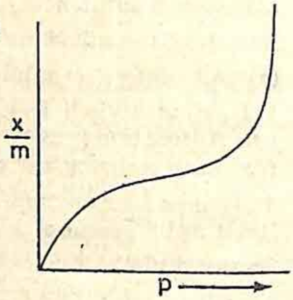
(b)



(c)



(d)



22.14 In the Langmuir adsorption isotherm, when $p \rightarrow 0$, the amount of substance adsorbed per gram of the adsorbent is proportional to

(a) p^2
(b) $1/p$
(c) p
(d) p^0

22.15 The kinetics of the decomposition of ammonia on the tungsten surface follows

(a) zero order
(b) first order
(c) second order
(d) third order

22.16 Retarded reactions are those

(a) in which the rate of the reaction is independent of pressure
(b) in which products are strongly adsorbed on the surface of the solid catalyst
(c) which are reversible under all conditions
(d) for which ΔG is positive

22.17 When the gas is only slightly adsorbed on the surface of the catalyst, the rate of decomposition is

(a) $-\dfrac{dp}{dt} = kp$

(b) $-\dfrac{dp}{dt} = kp^2$

(c) $-\dfrac{dp}{dt} = k$

(d) $-\dfrac{dp}{dt} = \dfrac{k}{p}$

22.18 The adsorption theory can explain the action of all these except

(a) heterogeneous catalysis
(b) catalytic poisons

(c) acid-base catalysis
(d) promoters

22.19 Catalytic poisons act by
(a) getting adsorbed on active centres on the catalyst surface
(b) chemical combination with any one of the reactants
(c) increasing the rate of the backward reaction
(d) making the products inert.

22.20 Which of the following is an example of a heterogeneous catalysed reaction ?
(a) $SO_2 + \frac{1}{2}O_2 \xrightarrow{NO} SO_3$
(b) $CH_3COOC_2H_5 \xrightarrow{H^+} CH_3COOH + C_2H_5OH$
(c) $H_2O_2 \xrightarrow{Pt} H_2O + \frac{1}{2}O_2$
(d) $CH_3CHO \xrightarrow{I_2\ \text{vapour}} CH_4 + CO$

22.21 The adsorption theory explains
(a) homogeneous catalysis
(b) acid-base catalysis
(c) heterogeneous catalysis
(d) enzyme catalysis

22.22 Which of the following is not an example of heterogeneous catalysis ?
(a) $SO_2 + \frac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$
(b) $RCH_3 + \frac{3}{2}O_2 \xrightarrow{CoBr_2} RCOOH + H_2O$
(c) Unsaturated oil + $H_2 \xrightarrow{Ni}$ Saturated oil
(d) $SO_2 + \frac{1}{2}O_2 \xrightarrow{NO} SO_3$

22.23 100 ml of 0.3 M acetic acid is shaken with 0.8 g wood charcoal. The final concentration of the solution after adsorption is 0.125 M. The weight of acetic acid adsorbed per gram of carbon is
(a) 1.050 g
(b) 0.0175 g
(c) 1.31 g
(d) 0.125 g

22.24 A substance which lowers the catalytic activity of a catalyst is called a/an
(a) autocatalyst
(b) negative catalyst
(c) promoter
(d) poison

22.25 The Langmuir theory of unimolecular adsorption is generally valid at
(a) low pressures and low temperatures
(b) low pressures and high temperatures
(c) high pressures and low temperatures
(d) high pressures and high temperatures

Type B: True or False

22.26 The term sorption is used for both the adsorption and absorption phenomena.

22.27 The substance which is adsorbed is called the adsorbent.

22.28 The phenomenon of adsorption occurs because the molecules at the surface of the solid are in a higher energy state.

22.29 For a substance to be an effective adsorbent, it must be in a finely divided state.

22.30 The heat of chemisorption is much higher than physical adsorption.

22.31 At very high pressures, adsorption generally becomes independent of pressure.

22.32 The extent of adsorption depends on the nature of the adsorbate and not on the adsorbent.

22.33 Generally, adsorption decreases with increase in temperature.

22.34 The Langmuir adsorption isotherm considers only a unimolecular layer of the adsorbate molecules.

22.35 In the Freundlich adsorption isotherm, $x/m = kp^n$, the value of n being more than 1.

22.36 Hydrogenation of an unsaturated oil over nickel is not an example of heterogeneous catalysis.

22.37 Heterogeneous catalysed reactions can be explained by the adsorption theory.

22.38 Adsorption is an irreversible process.

22.39 In retarded reactions, the products are more strongly adsorbed than the reactants.

22.40 Adsorption decreases surface energy.

Type C: Fill in the Blanks

22.41 In physical adsorption, the molecules of the adsorbate are held by ———— forces.

22.42 In the phenomenon of ————, the molecules of the substance are dispersed in the entire bulk of the other substance.

22.43 According to the Langmuir adsorption isotherm, when p is ———— adsorption becomes independent of pressure.

22.44 One such isotherm which takes into account the multimolecular layers of adsorption is ————.

22.45 Substances which lower the catalytic activity of a surface are called ————.

ANSWERS

Numerical Problems

22.1 $a = 1.896$ cm^3 g^{-1} bar^{-1}, $b = 0.146$ bar^{-1} *22.2* 344 m^2 g^{-1} *22.3* 5.265×10^{-4} mol g^{-1}, 1.685×10^{-2} g of oxygen/g, 11.79 cm^3 (STP) g^{-1} *22.4* $k = 2.06$, $n = 0.616$ *22.5* 1.25 bar

Quiz Questions

22.6 (a) *22.7* (a) *22.8* (b) *22.9* (b) *22.10* (a) *22.11* (d) *22.12* (c) *22.13* (c) *22.14* (c) *22.15* (a) *22.16* (b) *22.17* (a) *22.18* (c) *22.19* (a) *22.20* (c) *22.21* (c) *22.22* (d) *22.23* (c) *22.24* (d) *22.25* (b) *22.26* True *22.27* False *22.28* False *22.29* True *22.30* False *22.31* True *22.32* False *22.33* True *22.34* True *22.35* False *22.36* False *22.37* False *22.38* False *22.39* True *22.40* True *22.41* van der Waals *22.42* absorption *22.43* Very large *22.44* B.E.T. equation *22.45* catalytic poisons

23

Colloids and Macromolecules

Thomas Graham (1861) on the basis of diffusion studies drew a distinction between colloids (glue like, e.g. proteins, gums, etc.) and crystalloids (low molecular weight substances) and observed that the colloids did not diffuse through membranes while crystalloids did. This definition is no longer tenable as almost all substances can be brought to the colloidal state, although with great difficulty in some cases. A colloidal system consists of a dispersed phase and a continuous phase (also known as dispersion phase). The dispersed and continuous phase may be present in the gaseous, liquid or solid state. Out of the nine possibilities (3×3) only the combination gas in gas does not lead to a colloidal system while the remaining eight combinations exist as given below:

TABLE 23.1 *Different types of colloidal systems*

Dispersed phase	*Dispersion phase*	*Common name*	*Example*
Liquid	Gas	Aerosol of liquid particles	Mist
Liquid	Liquid	Emulsion	Milk
Liquid	Solid	Solid emulsion	Jellies
Solid	Gas	Aerosol of solid particles	Smoke
Solid	Liquid	Colloidal suspension or sols	Blood
Solid	Solid	Solid suspension	Certain precious stones
Gas	Liquid	Foam	Whipped cream
Gas	Solid	Solid foam	Polystyrene foam

23.1 CHARACTERISTICS OF COLLOIDAL PARTICLES AND DIFFERENT TYPES OF COLLOIDS

The size of colloidal particles (particles of the dispersed phase) lies in the range 1–1000 nm (10–10,000 Å or 0.001 to 1 μm) and therefore these have large interfaces with the continuous phase per gram of colloidal material. The colloidal particle may have the same structure as the bulk material (metals, insoluble salts, etc.) or may be obtained by the aggregation of small molecules in an appropriate solvent. For example, sodium stearate in water forms a colloidal system by the aggregation of stearate ions. Solutions of natural or synthetic macromolecules are true solutions but behave like colloids as the size of a single molecule lies in the colloidal range. Such systems are thermodynamically stable as the free energy of their solution is negative. On the other hand, many colloidal suspensions are metastable as their free energy decreases when aggregation of the colloidal particles takes place.

EXAMPLE 23.1 A gold sol contains 0.193 g of gold per dm³. The particles are spherical in shape with radius of 120 nm. How many particles are present in 10^{-14} m³ of the sol? What is the interfacial area of the gold particles in 1 m³ of the sol? The density of gold is 19.3 g cm^{-3}.

Solution Amount of gold present in 1 dm³ of sol = 0.193 g

$$\text{Volume of gold present in 1 dm}^3\text{ of sol} = \frac{0.193\text{ g}}{19.3\text{ g cm}^{-3}}$$

$$= 0.01\text{ cm}^3 = 0.01\times10^{-6}\text{ m}^3$$

$$\text{Radius of gold particle} = 120\text{ nm} = 120\times10^{-9}\text{ m}$$

$$\text{Volume of gold particle} = 4/3\ \pi r^3 = 4/3\times3.14\times(120\times10^{-9})^3$$

$$= 7.2\times10^{-21}\text{ m}^3$$

Number of particles present in 1 dm³ of sol

$$= \frac{\text{Total volume of gold in dm}^3\text{ of sol}}{\text{Volume of 1 particle of gold}}$$

$$= \frac{0.01\times10^{-6}\text{ m}^3}{7.2\times10^{-21}\text{ m}^3} = 1.38\times10^{12}\text{ particles}$$

$$\text{Number of particles present in 1 m}^3\text{ of sol} = 1.38\times10^{12}\times10^3 = 1.38\times10^{15}$$

$$\text{Number of particles present in }10^{-14}\text{ m}^3 = 1.38\times10^{15}\times10^{-14}$$

$$= 13.8\approx14\text{ particles}$$

$$\text{Surface area of 1 particle} = 4\pi r^2 = 4\times3.14\ (120\times10^{-9})^2 = 18.08\times10^{-14}\text{m}^2$$

$$\text{Surface area of }1.38\times10^{15}\text{ particles} = 18.08\times10^{-14}\times1.38\times10^{15}\text{ m}^2$$

$$= 249.5\text{ m}^2$$

It can be seen that the interfacial area is extremely large.

EXAMPLE 23.2 A soap ($C_{17}H_{35}COONa$) solution becomes a colloidal sol at a concentration of 1.2×10^{-3} M. On the average, 2.4×10^{13} colloidal particles are present in 1 mm³. What is the average number of stearate ions in one colloidal particle (micelle)?

Solution The colloidal particle here is formed by the aggregation of stearate ions in such a way that their polar groups are oriented towards water and the hydrocarbon chains are inwards.

In one litre of solution we have 1.2×10^{-3} M of sodium stearate. Therefore,

$$\text{Number of sodium stearate molecules in 1 litre} = 1.2\times10^{-3}\times6.02\times10^{23}$$

$$= 7.2\times10^{20}$$

$$\text{Number of molecules per mm}^3 = \frac{7.2\times10^{20}}{1000\times1000} = 7.2\times10^{14}$$

$$\text{Number of colloidal particles per mm}^3 = 2.4\times10^{13}$$

$$\text{Number of molecules per colloidal particle} = \frac{7.2\times10^{14}}{2.4\times10^{13}} = 30$$

i.e. on the average, the soap micelle is an aggregation of 30 stearate ions.

EXAMPLE 23.3 One gram of a water-insoluble substance of density 0.8 g cm^{-3} is dispersed in 2 *l* of water, leading to the formation of a colloidal sol containing 10^{13} particles of spherical shape per mm^3. Determine the radius of the particle.

Solution

1 mm^3 of sol contains 10^{13} particles
1 cm^3 of sol contains $10^{13}\times10^3 = 10^{16}$ particles
2 *l* of sol contains $10^{16}\times2\times10^3 = 2\times10^{19}$ particles

$$\text{Mass of substance dispersed} = 1.0 \text{ g}$$

$$\text{density} = 0.8 \text{ g cm}^{-3}$$

$$\text{Volume of dispersed substance} = \frac{1.0 \text{ g}}{0.8 \text{ g cm}^{-3}} = 1.25 \text{ cm}^3$$

This is also the volume of 2×10^{19} particles. Hence,

$$\text{Volume of 1 particle} = \frac{1.25}{2\times10^{19}} \text{ cm}^3 = 0.625\times10^{-19} \text{ cm}^3$$

$$= 62500 \text{ Å}^3$$

$$\text{Now, volume} = \frac{4}{3}\pi r^3 = 62500 \text{ Å}^3$$

$$\therefore\ r = \left[\frac{3}{4}\pi \times 62500\right]^{\frac{1}{3}} \text{Å} = 24.62 \text{ Å}$$

23.2 LYOPHILIC AND LYOPHOBIC SOLS

Colloidal dispersions of solids in liquids are called sols. These are divided into the following two categories, depending on the affinity of the colloidal particles for the dispersion medium.

Lyophilic (Liquid-loving) Sols

In these types of sols there is strong interaction between colloidal particles and the liquid. They are true solutions of macromolecules or aggregates of small molecules (e.g. soap micelles) and are easily formed when the components are shaken together. They are thermodynamically stable. When the dispersion medium is water, they are known as *hydrophilic sols*.

Lyophobic (Liquid-hating) Sols

These are generally dispersions of insoluble substances in liquids. The colloidal particles have very little interaction with the liquid and, due to their large interfacial area (Example 23.1), their formation is accompanied by an increase in their free energy. Therefore, lyophobic sols are thermodynamically unstable and would ultimately separate into bulk phases to attain the minimum interfacial area. However, due to charges on the colloidal particles, their rate of coagulation is very slow. The sol is kinetically stable, so much so that it can remain stable for years together. In water as dispersion medium, these are called *hydrophobic sols.*

Preparation and Purification of Sols

As mentioned earlier, lyophilic sols can be prepared by dissolving the solids in the liquid. If the starting components are pure, no further purification is needed. For the preparation of lyophobic sols, the following methods are generally used.

Dispersion Methods

In this method, the bulk material disintegrated to particles of colloidal dimensions in the presence of the dispersion medium. This is generally done by mechanical grinding in a colloid mill.

Condensation Methods

In this method, the colloid particles are formed from atoms, molecules or ions by a physical or a chemical process. This include:

(i) *Bredig arc method* This method is suitable for metal sols. The evaporation of metals is caused by striking an electric arc between two metal electrodes dipping in a suitable liquid medium. The vapours, containing mostly atoms, condense in the liquid to give the sols.

(ii) *Chemical reactions* Certain chemical reactions lead to insoluble products which aggregate to give colloidal sols, e.g. preparation of As_2S_3 sol by reaction between H_2S and H_3AsO_3, and preparation of gold sol by reduction of gold chloride.

(iii) *Change of solvent* The solution of a substance is prepared in a liquid in which it is easily soluble. To this is added a liquid which leads to decrease in solubility and formation of a colloidal sol. For example, sulphur sol is prepared by dissolving it in alcohol and then adding water.

Purification of Sols

Depending upon the method of preparation, a sol may contain impurities, e.g. soluble electrolytes or non-electrolytes. Since these affect the stability and other properties of the sol, it is necessary to get rid of them. Any of the following methods can be used for this purpose.

Dialysis The sol is suspended in a bag of a suitable membrane (e.g. cellophane, cellulose acetate, etc.) through which small molecules are permeable. This is surrounded by distilled water (or any other appropriate liquid). The colloidal particles are left behind. A constant flow of distilled water is maintained around the bag.

Electrodialysis If the impurity is an electrolyte, the dialysis process can be quickened by applying an electric field across the membrane. The ions move faster under the field and get out of the membrane quickly.

Ultrafiltration Colloidal particles pass through ordinary filter paper. However, the hole size of an ordinary filter paper can be decreased by impregnating the filter paper with suitable materials. The filter paper thus prepared is known as an ultrafilter paper. Filtration through this removes impurities, leaving the colloid on the paper. This may be diluted by the dispersion liquid.

23.3 PROPERTIES OF COLLOIDAL SOLS

The following are the important properties of colloidal sols:

Colligative Properties

It can be seen from Examples 23.1 to 23.3 that the number of colloidal particles per litre of the sol is relatively much lesser than in a true solution. Therefore, the sols boil and freeze at almost the same temperature as the pure dispersion medium and lowering of its vapour pressure is almost negligible. The osmotic pressure for colloidal systems, though smaller than true solutions, is measurable and gives information regarding the number of particles present per kilogram of the dispersion medium.

Optical Properties

A colloidal sol seems transparent to the naked eye. However, when a beam of light is passed through a colloidal solution, the path of the light beam becomes visible. The visibility is due to the scattering of light from the surfaces of colloidal particles. This phenomenon is called the *Tyndall effect.*

This has been used by Zsigmondy in devising the ultra-microscope to determine the size of colloidal particles. The scattering of light by the colloidal particles has been used to determine the molecular weights/shapes and sizes of colloidal particles and macromolecules.

Dynamic Properties

Colloidal particles, when observed under a microscope, show a ceaseless random motion in short straight paths of different lengths and direction. This phenomenon was first observed by Brown, on pollen grains, and is called Brownian motion. This is due to the bombardment of colloidal particles by molecules of the medium. The mean square displacement; $<x^2>$ of a particle in time t is given by the Einstein equation;

$$<x^2> = t\,\frac{k_b T}{3\eta\pi r} \qquad (23.1)$$

where k_b is the Boltzmann constant, T the temperature, η the viscosity of the medium, and r the radius of the particle. If $<x^2>$ is measured for a particle by noting the value of x^2 at equal intervals of times, then, using Eq. (23.1), k_b can be determined if r is known. Equation (23.1) was used to determine Avogadro's number as $k_b = \frac{R}{N_a}$.

EXAMPLE 23.4 The root mean square displacement of colloidal particles of radius 2.1×10^{-5} cm, in water at 17°C, is 10.6×10^{-4} cm in 60 s. Calculate Avogadro's number if the viscosity of water at 17°C is 0.011P. (Gas constant, $R = 8.27 \times 10^7$ ergs mol^{-1} K^{-1}).

Solution

$$<x^2> = \frac{k_b T}{3\eta\pi r}$$

Substituting values,

$$(10.6 \times 10^{-4})^2 = \frac{k_b \times 290 \times 60}{3 \times 0.011 \times 3.14 \times 2.1 \times 10^{-5}}$$

Solving

$$k = 1.405 \times 10^{-16} \text{ erg mol}^{-1} \text{ K}^{-1}$$

But $$N_a = \frac{R}{k_b} = \frac{8.27 \times 10^7}{1.405 \times 10^{-16}} = 5.89 \times 10^{23}$$

Surface Tension and Viscosity

The surface tension and viscosity of the lyophobic sol is nearly the same as that of the dispersion liquid, but those of lyophilic sols is quite different. The intrinsic viscosity (see p. 520) gives information about the molecular size per mass of the colloidal particles or macromolecules.

Electrical Properties

Colloidal particles in a dispersion medium carry electric charges. Some of these are positively charged (ferric hydrous oxide sol) while others (arsenious sulphide sol) are negatively charged. In the silver chloride sol, particles may be either positively or negatively charged, depending upon the method of preparation. The origin of charge may be due to the following reasons.

(a) *Direct ionization of surface groups* Proteins contain many acidic and basic groups which are ionizable. Therefore, depending upon the acidity of the medium, the particles in the protein sol can be either positively or negatively charged.

(b) *Selective adsorption of ions* The particles specifically adsorb +ve or −ve ions present in the medium, and hence acquire the charge of the adsorbed ion.

Coagulation of Lyophilic Sols

Lyophilic sols are stable due to strong interactions between the colloidal particles and the molecules of the dispersion medium. The lyophilic sol particles (proteins and polymer molecules like starch, etc.) are highly solvated and will remain stable unless a competing agent for the solvent molecules is introduced in the sol. This can be done in the following two ways:

(a) Addition of electrolytes to lyophilic colloidal sols leads to a competition for solvent molecules, both by ions of the electrolyte and the colloidal particles. Therefore, on addition of sufficient amounts of electrolytes, the sols coagulate. This is termed the salting out of sols.

(b) Lyophilic sols can also be coagulated by introducing a second liquid which interacts strongly with the dispersion medium.

Coagulation of Lyophobic Sols

If the particles in lyophobic sols are not charged, they have only attractive van der Waals forces and would coalesce on every collision, leading to fast coagulation. However, as explained earlier, the colloidal particles are charged and have electrical double layers. The interaction potential energy depends on the distance and is a net result of the van der Waals attractive potential and the repulsive potential due to the over lap of charge clouds surrounding colloidal particles. This leads to a potential energy barrier between the colliding particles, which, therefore, do not coalesce. Thus the stability of lyophobic sols is due to the electrical double layer. On addition of an electrolyte to the sol, the concentrations of counter-ions and co-ions increase in the sol and the thickness of the double layer decreases. The particles can now come nearer without overpowering the repulsive forces at large distances. At short distances, the van der Waals forces are strong enough to cause flocculation. It has been found that the greater the charge of the counter-ion added, the greater is the power (low concentration) to cause coagulation. This is known as the *Hardy–Schulze rule*. For example, the coagulation power of negatively charged particles (e.g. As_2S_3) is in the order $Al^{3+} > Ba^{2+} > Na^+$, while for positively charged particles (ferric hydrous oxide the coagulation power is in the order $PO_4^{3-} > SO_4^{2-} > Cl^-$.

The *flocculation value* of an electrolytic is defined as the minimum number of milli-moles of an electrolyte per litre of the sol required for its coagulation.

EXAMPLE 23.5 In a coagulation experiment, 5 ml of As_2S_3 sol is mixed with distilled water and a 0.1 M solution of sodium chloride so that the total volume is 10 ml. It has been found that all tubes containing more than 4.7 ml of sodium chloride coagulate within 5 minutes. What is the flocculation value of sodium chloride for As_2S_3 sol ?

Solution A minimum of 4.7 cm^3 of electrolyte in 10 cm^3 is required to coagulate the sol. The molarity of sodium chloride in the sol is

$$= \frac{4.7 \times 0.1}{10} = 0.047$$

This means that a minimum of 0.047 moles of NaCl should be present in 1 litre so that coagulation takes place. Therefore, by definition, the coagulation value is 0.047 × 1000 moles.

23.5 PROTECTION OF COLLOIDS

The coagulation of lyophobic colloids by electrolytes can be reduced by the addition of some lyophilic sols. The added lyophilic sols are called *protective colloids* and their action in stabilizing lyophobic sols is called *protective action.*

The protection of colloids is of great industrial importance. The protective power of each protecting colloid is described in terms of the *gold number* (introduced by Zsigmondy). The gold number is defined as the number of milligrams of the lyophilic substance required to prevent coagulation of 10 ml of a given gold sol (containing 0.5 to 0.018 g of gold per litre) on adding 1 ml of a 10 per cent solution of sodium chloride. The coagulation of a gold sol is indicated by a change in colour from red to blue. Obviously, the smaller the gold number the larger will be its protective power.

23.6 EMULSIONS

These are colloidal systems in which both the dispersed phase and the dispersion medium are liquids which are immiscible. In most cases, one of the liquid phases is water and the other an oil. Accordingly, we come across two types of emulsions—oil-in-water and water-in-oil.

Substances which make emulsions stabler are called emulsifiers. These are generally long-chain molecules with polar groups. For example, soaps, proteins and long-chain sulphonic acids act as emulsifying agents. The stabilization of an emulsion by means of an emulsifier is called emulsification.

23.7 GEL

A gel is a colloidal system in which a liquid is dispersed in a solid. Under certain conditions, the lyophilic sol may be coagulated to give a semi-rigid jelly like mass which encloses all the liquid present in the sol. The product so obtained is called a gel and the process is called *gelation.* Gels are of two types—elastic gels (agar agar, gelatin) and non-elastic gels (silica gel).

23.8 MACROMOLECULES

Macromolecules or polymers are substances with molecular masses greater than 10,000. These consist of hundreds or thousands of smaller molecules joined together. The smaller molecule is called a monomer and is the repeat unit. These may be arranged linearly as links in a chain (linear polymer), or interconnected by a three-dimensional network. The number of repeat units in a polymer is called its degree of polymerization. Polymers are of two types:

(a) *Natural polymers* Examples are proteins, polysaccharides, resins, rubber, silk, etc.

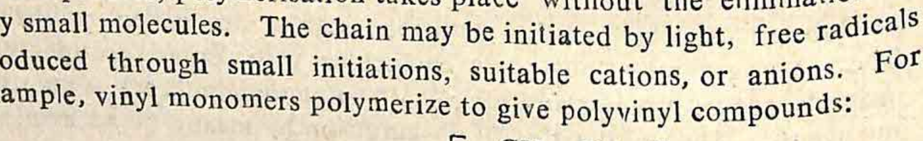
(b) *Synthetic polymers* A few examples of synthesized polymers are polyethylene, nylon, dacron, teflon, polyvinyl chloride, etc.

23.9 MECHANISM OF POLYMERIZATION

Carothers (in 1929) classified polymerization reactions as condensation and addition polymerization.

Condensation Polymerization

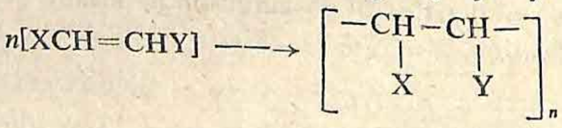
In this process, polymers are formed by reactions in which small molecules such as H_2O or NH_3 are eliminated from the reactant monomer molecules. For example, polyester is formed by the condensation of glycols with dibasic acids by the elimination of water:



$$n[\mathrm{HO{-}R{-}OH}]+n[\mathrm{HOOC{-}R'{-}COOH}] \longrightarrow \mathrm{HO}[-\mathrm{R}-\mathrm{O}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{R'}-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}-\mathrm{O}-]_n\mathrm{H}+(2n-1)\mathrm{H_2O}$$

Addition Polymerization

In this process, polymerisation takes place without the elimination of any small molecules. The chain may be initiated by light, free radicals produced through small initiations, suitable cations, or anions. For example, vinyl monomers polymerize to give polyvinyl compounds:



$$n[\mathrm{XCH{=}CHY}] \longrightarrow \left[\begin{array}{cc} -\mathrm{CH}- & \mathrm{CH}- \\ | & | \\ \mathrm{X} & \mathrm{Y} \end{array}\right]_n$$

23.10 MOLECULAR WEIGHTS OF POLYMERS

The molecular weight of a single polymer molecule can be obtained by multiplying the molecular weight of the repeat unit by its degree of polymerization. Generally, a polymer sample contains macro molecules with different degrees of polymerization. Therefore, the sample has to be characterized by an average molecular weight. There are two important averages.

Number–Average Molecular Weight ($\overline{M}_n$)

If $n_1, n_2, n_3, \ldots$ are the number of molecules with molecular weights $M_1, M_2, M_3, \ldots$, respectively, then the number average molecular weight is

$$\overline{M}_n = \frac{n_1M_1+n_2M_2+n_3M_3+\ldots}{n_1+n_2+n_3+\ldots} \text{ a.m.u.}$$

$$\text{or} \qquad \overline{M}_n = \frac{\Sigma\, n_i\, M_i}{\Sigma\, n_i} = \Sigma\, x_i\, M_i$$

where n_i is the number of molecules of the *i*th type with molecular weight M_i, and x_i the mole fraction of polymer of molecular weight M_i.

Weight-Average Molecular Weight ($\overline{M_w}$)

If $m_1, m_2, m_3, \ldots$ are the masses of species with molecular weights $M_1, M_2, M_3, \ldots$, respectively ($m_i = n_iM_i$ where n_i is the number of molecules with molecular weight M_i), then the average molecular weight is

$$\overline{M}_w = \frac{m_1M_1+m_2M_2+m_3M_3+\ldots}{m_1+m_2+m_3+\ldots}$$

$$\text{or} \qquad M_w = \frac{\Sigma\, m_i\, M_i}{\Sigma\, m_i}$$

$$\text{But} \qquad m_i = n_iM_i$$

$$\therefore \qquad \overline{M}_w = \frac{\Sigma\, n_i\, M_i^2}{\Sigma\, n_i\, M_i} = \frac{\Sigma\, x_i\, M_i^2}{\Sigma\, x_i\, M_i}$$

EXAMPLE 23.6 A sample of polymer contains 5, 25, 40 and 30 per cent molecules of the polymer with molecular weights 10,000, 12,000, 13,000 and 15,000. What is the mole fraction of each type of polymer molecule and what are the number and weight-average molecular weights of the polymer sample ?

Solution

$$\text{Mole fraction, } x_i = \frac{\text{Number of molecules of type } i}{\text{Total number of molecules}}$$

In this case, the number of molecules is 100.
Therefore, their mole fractions are 5/100, 25/100, 40/100, and 30/100, i.e. 0.05, 0.25, 0.4 and 0 3.

$$\begin{aligned}\overline{M}_n &= \Sigma\, x_i\, M_i\\ &= 0.05\times 10{,}000+0.25\times 12{,}000+0.4\times 13{,}000+0.3\times 15{,}000\\ &= 500+3000+5200+4500 = 13200\end{aligned}$$

$$\bar{\ }_w = \frac{\Sigma\, x_i\, M_i^2}{\Sigma\, x_i\, M_i} = \frac{0\ 05(10{,}000)^2+0.25(12{,}000)^2+0.4(13000)^2+0.3(15000)^2}{13200}$$

$$= \frac{5\times10^6+36\times10^6+67.6\times10^6+67.5\times10^6}{13200}$$

$$= \frac{176.1\times10^6}{13.2\times10^3} = 13.34\times10^3 = 13340$$

23.11 METHODS FOR DETERMINATION OF MOLECULAR WEIGHTS

The common methods are as follows.

Viscosity Method

If η is the viscosity of the polymer solution at concentration c, and η_0 is the viscosity of the pure solvent, the terms relative, specific and reduced viscosities are defined as

$$\text{Relative viscosity } (\eta_r) = \frac{\eta}{\eta_0} \tag{23.3}$$

$$\text{Specific viscosity } (\eta_{sp}) = \eta_r - 1 = \frac{\eta-\eta_0}{\eta_0} \tag{23.4}$$

$$\text{Reduced viscosity } (\eta_{red}) = \frac{\eta_{sp}}{c}$$

where c is the concentration (g/100 ml) of the polymer in the solution. The intrinsic viscosity is the reduced viscosity when concentration approaches zero, i.e.

$$\eta_{int} = \underset{c\to0}{\text{limit}}\left(\frac{\eta_{sp}}{c}\right)$$

Thus, η_{red} for several concentrations of polymers are determined and η_{int} obtained by the intercept of the curve between η_{red} and c. The intrinsic viscosity is related to molecular weight M as

$$\eta_{int} = k\,M^{\alpha} \tag{23.5}$$

where k and α are constants. Their values can be determined by drawing a graph between log η_{int} and log M for solutions of polymers of known M. The slope of the line is α and the intercept gives log k. The constants are specific for a particular series of molecules. It corresponds to the weight-average molecular weight when $\alpha = 1$.

Osmotic Method

The osmotic pressures (π) of solutions of different small concentrations (c) are determined with an osmometer. The osmotic pressure is related to molecular weight as

$$M = \frac{cRT}{\pi}$$

where c is the mass (g) of the solute dissolved in one litre of solution. A graph is then plotted between (π/c) and (c) so that the intercept for

$c = 0$ gives RT/M from which M can be calculated. This gives the number average molecular weight.

EXAMPLE 23.7 The osmotic pressure of nitrocellulose has been measured at various concentrations, at 27°C in acetone, and the following data obtained. Determine molecular weight of the nitrocellulose samples

C (g/l)	1.16	3.66	8.38	19.0
π (torr)	0.47	1.93	6.02	19.12

Solution

From the above data we obtain the value of π/c at different concentrations and draw a graph between π/c and c to obtain π/c at limiting zero concentration.

c	1.16	3.66	8.38	19.0
π/c	0.405	0.527	0.718	1.006

The limiting value of RT/M is obtained from the intercept at $c = 0$ and is equal to 0.335 torr l g^{-1}

$$\therefore \quad \frac{RT}{M} = 0.355 \text{ torr } l \text{ g}^{-1}$$

$$M = \frac{RT}{0.355}$$

The units of R should agree with the units of π/c.

$$M = \frac{0.082 \times 760 \times 300}{0.355}$$

$$M = 52665$$

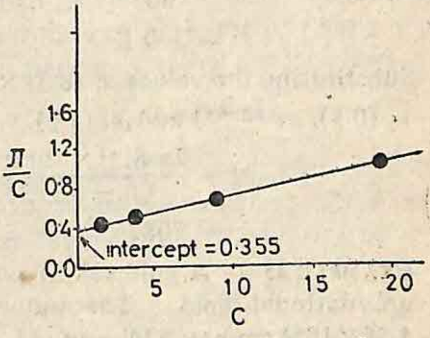


FIG. 23.1 *Graph of* π/c *and* c

Sedimentation Method

The rates of sedimentation of colloidal solutions can be accelerated by applying the ultracentrifugal technique. In the ultracentrifuge, there is an optical arrangement to determine the concentration of polymer molecules at different depths in the cell. There are two methods.

Sedimentation equilibrium An equilibrium distribution of the polymer molecules is obtained when the rate of diffusion from the bottom to tha top of the cell is equal to the rate at which the particles settle down. If c_1 and c_2 are the concentrations at depths x_1 and x_2. ρ is the density of the solvent, V the specific volume of solute and ω the angular velocity in radians per second, then molecular weight M is given by the relation,

$$M = \frac{2RT \ln \left(\dfrac{C_2}{C_1} \right)}{(1 - V\rho)\, \omega^2 \,(x_2^2 - x_1^2)}$$

The molecular weight obtained by this method is weight average.

Sedimentation velocity method In this method, a reference layer te macromolecules in the cell is chosen and the velocity (dr/dt) with which it moves towards the bottom, due to rotation, is determined. The molecular weight is

$$M = \frac{RTS}{D\,(1-\bar{v}\,\rho)}$$

where S is the sedimentation velocity dr/dt at depth r, T the temperature and D the diffusion coefficient.

EXAMPLE 23.8 A solution of a protein is rotated in an ultracentrifuge at 9000 revolutions per minute, at 300 K. The concentration of protein at distances 4.55 and 4.5 cm are 0.915 and 0.816 per cent, respectively. Calculate the molecular weight of protein if the average density of the solution is 0.999 g cm^{-3}. The specific volume of protein is 0.80 cm^3 g^{-1}.

Solution

$$M = \frac{2RT \ln C_1/C_2}{(1-\rho\,\bar{v}_2)\,\omega^2(x_2^2 - x_1^2)}$$

where ω is the angular velocity, i.e. the number of radians by which it rotates in one second

$$\omega = \frac{9000}{60} \times 2\pi = 942 \text{ s}^{-1}$$

$$T = 300 \text{ K}$$

Substituting the values $R\,(8.31\times10^7)$, $C_2\,(0.915)$, $C_1\,(0.816)$, $\rho\,(0.999)$, $\bar{v}_2\,(0.8)$, $x_2\,(4.55)$ and $x_1\,(4.5)$, we obtain

$$M = \frac{2\times8.31\times10^7\times300\times2.303\log(0.915/0.816)}{(1-0.999\times0.8)\,(942)^2\,(4.55^2-4.5^2)}$$

$$= 70826$$

EXAMPLE 23.9 A gold sol allowed to sediment to equilibrium under a gravitational field. The numbers of particles at height differences 4.58×10^{-3} cm are 334 and 41 at 290 K. If the density of gold is 19.3 g cm^{-3} and the radius of the gold particle is 62.5×10^{-7} cm, calculate the Avogadro number.

Solution

$$\ln\frac{n_1}{n_2} = \frac{N}{RT}\,v\,(\rho-\rho_0)\,g\,(h_2-h_1)$$

$$N = \frac{RT\ln\dfrac{n_1}{n_2}}{v(\rho-\rho_0)\,g\,(h_2-h_1)} = \frac{2.303\,RT\log\dfrac{n_1}{n_2}}{v(\rho-\rho_0)\,g\,(h_2-h_1)}$$

$$v = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\,(62.5\times10^{-7})^3 = 1.02\times10^{-15}$$

Substituting the values of $n_1(334)$, $n_2(41)$, $T(290)$, $\rho(19.3)$ $\rho_0(1)$, h_2-h_1 (4.58×10^{-3}), $R(8.31\times10^7)$ and $g(981)$, we obtain

$$N = \frac{2.303\times8.31\times10^7\times290\log(334/41)}{1.02\times10^{-15}\,(19.3-1)\,981\times4.58\times10^{-3}}$$

$$= 6.028\times10^{23}$$

EXAMPLE 23.10 For myoglobin in water at 20°C, the following data are known

$$\bar{v} = 0.741 \text{ cm}^3 \text{ g}^{-1}, \qquad S = 2.04 \times 10^{-13} \text{ s} \quad \text{and}$$
$$D = 11.3 \times 10^{-7}$$

Calculate the molecular weight of myoglobin.

Solution

$$M = \frac{RTs}{D(1-\bar{v}\rho)}$$

$$R = 8.31 \times 10^7 \text{ erg mol}^{-1} \text{ K}^{-1},\ T = 273+20 = 293\text{K},\ s = 2.04 \times 10^{-13} \text{ s}$$

$$D = 11.3 \times 10^{-7}, \qquad \bar{v} = 0.741 \text{ cm}^3 \text{ g}^{-1}, \quad \rho = 1 \text{ g cm}^{-3}$$

$$M = \frac{8.31 \times 10^7 \times 293 \times 2.04 \times 10^{-13}}{11.3 \times 10^{-7} (1-0.741 \times 1)}$$

$$= 16970$$

The molecular weight obtained by this method is weight average.

Light Scattering Method

This method involves the measurement of the intensity of the light scattered by polymer solutions. The fraction of light scattered per cm length of the solution through which it passes is called the *turbidity T*. It is related to intensity I as

$$I = I_0 \, e^{-Tl}$$

where I_0 is the intensity of the incident light and l is the length of the solution. Turbidities of different concentrations of solutions are determined in a suitable solvent. The molecular weight can be determined by the equation derived by Debye:

$$\lim_{c \to 0} H \frac{C}{T} = \frac{1}{M}$$

where H is a constant for a given polymer and a given dispersion medium, which depends upon the variation of refractive index concentration and the wavelength of the light used. The plot of $H\,C/T$ against C is extrapolated to get $1/M$. This method gives the weight-average molecular weight.

QUESTIONS

Numerical Problems

23.1 What is the total surface area if a cube of 1 cm edge is divided into cubes with edge equal to 10^{-6} cm ? What will be the edge of a single cube of the same surface area ?

23.2 A gold sol contains 0.24 g of gold per litre. When 10^{-4} m³ samples was examined under an ultramicroscope, on an average, 12 particles could be counted. Calculate the particle size if these are assumed to be spherical and the density of gold is 19.3 g cm^{-3}.

23.3 Calculate the surface area of a colloidal dispersion containing 2.3 g of a substance of density 4 6 if the particles are assumed to be spherical with radii of 25 nm.

23.4 A mercury sol has been prepared by dispersing 0.272 g of mercury in 2 *l* of solution, giving spherical particles of radius 12 nm. What is the total surface area of Hg particles present in 1 cm^3 of sol ?

23.5 The displacement of a particle in the x direction is observed under a microscope every 100 s. The following displacements were observed: $(-5.4, +3.5, -2, -0.5, +0.6, +3.2, -0.3, -3.6, +1.5, +0.4, -1.1, +2.7) \times 10^{-4}$ cm. Determine the root mean square displacement x^2 and the particle size, if $k = 1.38 \times 10^{-16}$ erg molecule^{-1} K^{-1}, $T=300$ K and $\eta=0.0105$ poise.

23.6 The flocculation value of $BaCl_3$ for negative silver iodide sol is 2.43. How many ml of 0.2 M $BaCl_2$ will be sufficient to start the coagulation of 400 ml of sol ?

23.7 A polymer sample has 50 and 100 g of polymers of molecular weight 12500 and 15000. Determine the number -and weight-average molecular weights of the sample.

23.8 A sample of polymer is dissolved in chlorobenzene and the osmotic pressure at various concentrations measured in terms of the height of chlorobenzene at 25°C. The density of chlorobenzene is 1.1 g cm^{-3}. The following data have been obtained.

Concentration (g l^{-1})	1.90	2.83	3.76	5.66
h (cm of chlorobenzene)	0.19	0.34	0.51	0.95

23.9 Pepsin has a molecular weight of 35500 and its specific volume is 0.750 cm^3 g^{-1}. Its sedimentation constant in water at 20°C is 3.3×10^{-13} s. Determine its diffusion coefficient in water at 20°C.

23.10 A polymer of molecular weight 140,000 has a specific volume of 0.8 cm^3 g^{-1} in a given solvent. A solution of the polymer of density 1.05 g cm^{-3}, is placed in an ultracentrifuge cell at 27°C and rotated at 10,000 rpm. Calculate the ratio of the concentrations of polymer at 5 and 5.2 cm.

QUIZ QUESTIONS

Type A: Multiple Choice

23.11 A system is said to be in the colloidal state if the particle size of the dispersed phase ranges from

(a) 1 to 10 Å
(b) 10 to 100 Å
(c) 10 to 10000 Å
(d) 1000 to 10000 Å

23.12 Which of the following statements is false regarding lyophilic sols ?

(a) The colloidal particles show a liking for the dispersion medium.
(b) These are generally easy to prepare,
(c) These are more stable than lyophobic sols.
(d) The stability of the sols is mainly due to the electrical double layer.

23.13 Which one of the following is the cause of Brownian movement of colloidal particles ?

(a) convection currents in the fluid
(b) bombardment by the molecules of the dispersion medium
(c) settling of dispersed phase under gravity
(d) thermal gradient in the medium

23.14 Colloids can be purified by

(a) peptization
(b) coagulation

(c) the Bredig arc method
(d) dialysis

23.15 Which of the following colligative, properties can be used to characterize colloidal particles

(a) lowering in vapour pressure
(b) elevation in boiling point
(c) depression in freezing point
(d) osmotic pressure

23.16 The process of removing dissolved impurities from a colloidal system, by means of diffusion through a suitable membrane under the influence of an electric field, is called

(a) electrosmosis
(b) electrodialysis
(c) electrophoresis
(d) peptization

23.17 The migration of positively charged colloidal particles, under an electrical field, towards the cathode is called

(a) cataphoresis
(b) electrosmosis
(c) sedimentation
(d) electrodialysis

23.18 Smoke is a dispersion of

(a) gas in gas
(b) gas in solid
(c) solid in gas
(d) liquid in gas

23.19 In the process of electrosmosis

(a) colloidal particles move towards the electrodes
(b) both, colloidal particles and dispersion medium, move
(c) only dispersion medium moves to carry the current
(d) positively charged colloidal particles move, but negatively charged particles remain stationary

23.20 When a strong beam of light is passed through a colloidal solution, the light will

(a) be reflected
(b) be scattered
(c) pass unchanged
(d) be dispersed

23.21 Which of the following electrolytes will be most effective in the coagulation of arsenious sulphide sol ?

(a) $NaNO_3$
(b) $MgSO_4$
(c) $AlPO_4$
(d) $K_4[Fe(CN)_6]$

23.22 The stabilization of the dispersed phase in a lyophobic sol is due to

(a) liking for the dispersion medium
(b) the surface tension of the medium
(c) the formation of an electrical layer between the two phases
(d) the viscosity of the medium

23.23 Which of the following will be most effective in the coagulation of $Fe(OH)_3$ sol ?

(a) NaCl
(b) $MgSO_4$
(c) $Mg_3(PO_4)_2$
(d) $AlCl_3$

23.24 A silver iodide sol was prepared by mixing KI and $AgNO_3$ solutions with the $AgNO_3$ in slight excess. Which of the following descriptions is correct regarding the sol particles ?

(a) negatively charged because of the excess of NO^-_3 ions
(b) positively charged because of the excess of Ag^+ ions in the AgI lattice
(c) negatively charged because I^- ions are adsorbed from the KI solution
(d) neutral

23.25 An emulsifier is an agent which
(a) stabilizes an emulsion
(b) homogenises an emulsion
(c) causes coagulation of an emulsion
(d) helps in the formation of an emulsion

23.26 A colloidal system in which a liquid is dispersed in a solid is called a/an
(a) emulsion (b) sol
(c) gel (d) precipitate

23.27 The gold numbers of some hydrophilic substances are:

gelatin	0.005–0.01
egg albumen	0.08–0.10
gum arabic	0.10–0.15
soluble starch	10–15

which of these will act best as a protective colloid ?
(a) gelatin (b) egg albumen
(c) soluble starch (d) gum arabic

23.28 The Tyndall effect was used by Zsigmondy to devise
(a) the ultramicroscope
(b) the ultracentrifuge
(c) the osmometer
(d) electrodialysis

23.29 Which of the following can act as a protective colloid ?
(a) gelatin
(b) silica gel
(c) oil-in-water emulsion
(d) all three

23.30 The process of passing of a precipitate into colloidal solution, on adding an electrolyte, is called
(a) dialysis (b) peptization
(c) electrophoresis (d) electrosmosis

23.31 The Tyndall effect is not observed in
(a) suspensions
(b) emulsions
(c) colloidal solutions
(d) true solutions

23.32 The colloidal solution of arsenic sulphide prefers to absorb
(a) NO_3^- (b) K^+
(c) S^{2-} (d) H^+

23.33 If a freshly formed precipitate of stannic oxide is peptised by a small amount of sodium hydroxide, the colloidal particles may be represented as
(a) $[SnO_2]Sn^{4+} : OH^-$
(b) $[SnO_2]SnO_3^{2-} : 2Na^+$
(c) $[SnO_2]Sn^{4+} : O^{2-}$
(d) $[SnO_2]Na^+ : OH^-$

23.34 Which of the following statements is not correct regarding the Stern theory of charge on colloidal particles ?
(a) The colloidal particle has a charge distribution at its surface.
(b) In the immediate vicinity of the colloidal particles there is an excess of counter ions.
(c) The greater the concentration and charge of ions in the diffused electrical double layer, the larger is the thickness of the layer.

(d) At large distances from the colloidal particles, the concentrations of co-ions and counter-ions are almost equal.

23.35 In emulsions, the dispersed phase and the dispersion medium are

(a) both solids
(b) both liquids
(c) both gases
(d) phase is liquid and medium is solid

23.36 If $n_1, n_2, n_3 \ldots$ are the number of molecules with molecular weights $M_1, M_2, M_3, \ldots$, respectively, then the weight-average molecular weight is

(a) $\dfrac{n_1M_1^2+n_2M_2^2+n_3M_3^2+\ldots,}{n_1+n_2+n_3+\ldots}$

(b) $\dfrac{n_1M_1^2+n_2M_2^2+n_3M_3^2+\ldots}{n_1M_1+n_2M_2+n_3M_3+\ldots}$

(c) $\dfrac{M_1^2+M_2^2+M_3^2+\ldots}{n_1+n_2+n_3+\ldots}$

(d) $\dfrac{n_1M_1+n_2M_2+n_3M_3+\ldots}{n_1+n_2+n_3+\ldots}$.

23.37 Which of the following methods gives the number-average molecular weight of a polymer?

(a) light scattering method
(b) osmotic method
(c) sedimentation equilibrium method
(d) viscosity method

23.38 Which of the following is a natural polymer

(a) nylon
(b) leucite
(c) cellulose
(d) polystyrene

23.39 Which of the following statements is not correct regarding the structure of DNA?

(a) it has a double helix structure
(b) there are hydrogen bonds in its structure
(c) unlike RNA, there is no fixed ratio of bases in DNA
(d) the code for protein synthesis is given by the sequence of bases in DNA

23.40 For monodisperse systems,

(a) $\overline{M}_n > \overline{M}_w$
(b) $\overline{M}_w > \overline{M}_n$
(c) $\overline{M}_n = \overline{\ }_w$
(d) $\overline{M}_n \geqslant \overline{M}_w$

23.41 The following distribution of molecular weights has been found in a polymer sample

n_i	5	10	10	10	20	5	5
M_i	1000	2000	5000	10000	12000	15000	20000

The number-average molecular weight is

(a) $\dfrac{5000+20000+50000+100000+240000+750000+100000}{65}$

(b) $\dfrac{1000+2000+5000+10000+12000+15000+20000}{65}$

(c) $\dfrac{5(1000)^2+10(2000)^2+10(5000)^2+10(10000)^2+20(12000)^2+5(15000)^2+5(2000)^2}{65}$

(d) $\dfrac{5(1000)^2+10(2000)^2+10(5000)^2+10(10000)^2+20(12000)^2+5(15000)^2+5(2000)^2}{5\times1000+10\times2000+10\times5000+10\times10000+20\times12000+5\times15000+5\times20000}$

23.42 The intrinsic viscosity is related to the molecular weignt (M) by the relation (k and α are constants)

(a) $\eta_{\text{int}} = kM^{\alpha}$
(b) $\eta_{\text{int}}/M = K\alpha$
(c) $\eta_{\text{int}} = kM\ e^{\alpha}$
(d) $\eta_{\text{int}} = ke^{\alpha M}$

23.43 Which of the following methods does not give the weight-average molecular weight ?

(a) sedimentation equilibrium
(b) sedimentation velocity
(c) light scattering
(d) osmotic method

23.44 In the osmotic method for the determination of molecular weight of polymers, molecular weight can be calculated from the intercept of the

(a) π versus c graph
(b) π/c versus c graph
(c) π/c versus RT/M graph
(d) π/c versus l/M graph

23.45 A colloidal system in which both the dispersion phase and dispersed phase are liquid is

(a) smoke
(b) emulsion
(c) whipped cream
(d) mist

Type C: True or False

23.46 In colloidal dispersions, the size of the particles of the dispersed medium lies in the range 1 mμ to 1 μ.

23.47 The Bredig arc method is particularly suitable for preparing colloidal sols of metals.

23.48 Brownian movement of colloidal particles is due to convection currents in the fluid.

23.49 The Stern layer in colloidal systems contains ions with charges opposite to the fixed layer.

23.50 Electrophoretic velocity is inversely proportional to zeta potential.

23.51 The smaller the gold number of a substance, the larger will be its protective power.

23.52 Colloidal systems in which both the dispersed phase and dispersion medium are liquids are called gels.

23.53 The osmotic pressure method gives the number-average molecular weight of a polymer.

23.54 Intrinsic viscosity is the reduced viscosity when concentration approaches zero.

23.55 Except for monodisperse systems, the weight-average molecular weight is less than the number-average molecular weight.

23.56 Lyophilic sols are stable due to strong interactions between colloidal particles and solvent molecules.

23.57 The flocculation value of arsenious sulphide sol is independent of the anion.

23.58 Lyophobic sols, in contrast to lyophilic sols, are easily coagulated on addition of small amounts of electrolytes.

23.59 Oil-in-water type emulsions generally have low conductance values as compared to those of water-in-oil type emulsions.

23.60 The light scattering method gives the weight-average molecular weight.

Type C: Fill in the Blanks

23.61 The protective power of protecting colloids is described in terms of the ————.

23.62 Substances which make emulsions stabler are called ————.

23.63 The flocculation value ———— as the charge on the cation increases, for negatively charged colloids.

23.64 The ———— average molecular weight gives too much weightage to lower molecular weight species.

23.65 The migration of colloidal particles, under electrical fields, towards the electrodes is called ————.

23.66 Colloidal dispersions in which the dispersion medium is liquid are called ————.

23.67 Colloidal particles exhibit ———— due to scattering of light.

23.68 Smoke is a dispersion of ———— in ————.

23.69 The number-average molecular weight of a polymer can be obtained by the ———— method.

23.70 If a sol is prepared by peptising a freshly formed precipitate of stannic oxide with a small amount of hydrochloric acid, the diffused layer will contain an excess of ———— charged ions.

ANSWERS

Numerical Problems

23.1 6×10^6 cm^2. edge of the cube = 10^2 cm *23.2* 120 nm *23.3* 59.97×10^4 cm^2 *23.4* 25.01 cm^2 *23.5* $<x^2> = 6.68\times10^{-4}$ cm, $r = 9.38\times10^{-5}$ cm *23.6* 1.95 ml *23.7* $M_n = 1406.25$ and $M_w = 14167$ *23.8* $M_n = 395878$ *23.9* $D = 9\times10^{-7}$ cm^2 s^{-1} *23.10* $C_2/C_1 = 1.775$

Quiz Questions

23.11 (c) *23.12* (d) *23.13* (b) *23.14* (d) *23.15* (d) *23.16* (b) *23.17* (a) *23.18* (c) *23.19* (c) *23.20* (b) *23.21* (c) *23.22* (c) *23.23* (c) *23.24* (b) *23.25* (a) *23.26* (c) *23.27* (a) *23.28* (a) *23.29* (a) *23.30* (b) *23.31* (d) *23.32* (c) *23.33* (b) *23.34* (c) *23.35* (b) *23.36* (c) *23.37* (b) *23.38* (c) *23.39* (c) *23.40* (c) *23.41* (a) *23.42* (a) *23.43* (d) *23.44* (b) *23.45* (b) *23.46* True *23.47* True *23.48* False *23.49* False *23.50* True *23.51* True *23.52* False *23.53* True *23.54* True *23.55* False *23.56* True *23.57* True *23.58* True *23.59* False *23.60* False *23.61* gold number *23.62* emulsifiers *23.63* decreases *23.64* number *23.65* electrophoresis *23.66* sols *23.67* Tyndall effect *23.68* solid, gas *23.69* osmotic pressure *23.70* negatively

Appendix

SOME IMPORTANT FUNDAMENTAL CONSTANTS

Quantity	Symbol	Value
1. Atomic mass unit	m_u	1.66056×10^{-27} kg
2. Avogadro number	N_a	6.02205×10^{23} mol^{-1}
3. Boltzmann constant	k_b	1.38066×10^{-23} J K^{-1}
4. Elementary charge	e	1.60219×10^{-19}C
5. Faraday constant	F	9.64846×10^{4} C mol^{-1}
6. Gas constant	R	8.31441 J K^{-1} mol^{-1}
7. Gravitational constant	G	6.6723×10^{-11} N m^{2}kg^{-2}
8. Mass of electron	m_e	9.10953×10^{-31} kg
9. Mass of proton	m_p	1.67265×10^{-27} kg
10. Mass of neutron	m_n	1.67495×10^{-27} kg
11. Planck's constant	h	6.626×10^{-34} J s
12. Rydberg constant	R_z	1.09737×10^{5} cm^{-1}
13. Speed of light in vacuum	c	2.997925×10^{8} m s^{-1}
14. Vacuum permittivity	ϵ_0	8.85419×10^{-12} J^{-1} cm^2 m^{-1}

LIST OF PREFIXES

Factor	Symbol	Name	Factor	Symbol	Name
10^{-1}	d	deci	10	da	deca
10^{-2}	c	centi	10^{2}	h	hecto
10^{-3}	m	milli	10^{3}	k	kilo
10^{-6}	μ	micro	10^{6}	M	mega
10^{-9}	n	nano	10^{9}	G	giga
10^{-12}	P	pico	10^{12}	T	tera
10^{-15}	f	femto	10^{15}	P	peta
10^{-18}	a	atto	10^{18}	E	exa

THE DERIVED SI UNITS OF SELECTED PHYSICAL QUANTITIES

Physical quantity	Name	Symbol for SI unit	Definition of SI unit
Force	newton	N	$\mathrm{kg\ m\ s^{-2}}$
Pressure	pascal	Pa	$\mathrm{kg\ m^{-1}s^{-2}=N\ m^{-2}}$
Energy	joule	J	$\mathrm{kg\ m^{2}s^{-2}}$
Power	watt	W	$\mathrm{kg\ m^{2}s^{-3}=J\ s^{-1}}$
Electric charge	coulomb	C	$\mathrm{A\ s}$
Electric potential differenc	volt	V	$\mathrm{kg\ m^{2}s^{-3}A^{-1}=J\ A^{-1}s^{-2}}$
Electric resistance	ohm		$\mathrm{kg\ m^{2}s^{-3}A^{-2}=V\ A^{-1}}$
Electric conductance	siemens	S	$\mathrm{kg^{-1}m^{-2}s^{3}A^{2}=V^{-1}\ A}$
Electric capacitance	farad	F	$\mathrm{A^{2}s^{2}kg^{-1}m^{-2}=A\ s\ V^{-1}}$
Magnetic flux	weber	Wb	$\mathrm{kg\ m^{2}s^{-1}=A^{-1}V\ s}$
Inductance	henry	H	$\mathrm{kg\ m^{2}s^{-2}A^{-2}=V\ A^{-1}s}$
Magnetic flux density	tesla	T	$\mathrm{kg\ s^{-2}A^{-1}V=\ s\ m^{-2}}$
Luminous flux	lumen	Lm	$\mathrm{Cd\ sr}$
Illumination	lux	Lx	$\mathrm{Cd\ sr\ m^{-2}}$
Frequency	hertz	Hz	$\mathrm{s^{-1}}$

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